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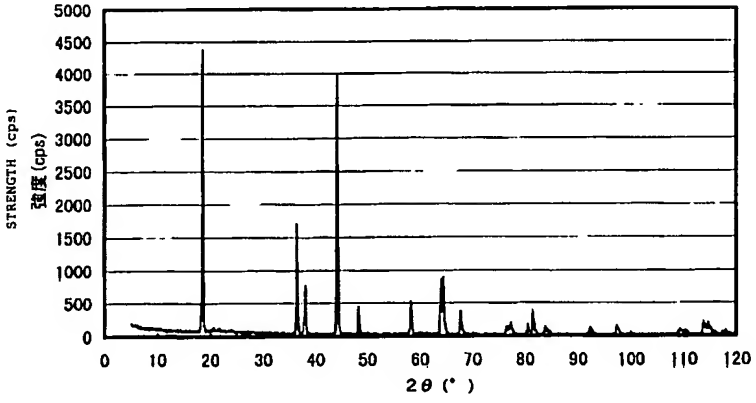
(54) Title: POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY CELL COMPRISING THE SAME

(54) 発明の名称: 正極活物質およびこれを用いた非水電解質二次電池



(57) Abstract: A positive electrode active material for producing a nonaqueous electrolyte secondary cell exhibiting an excellent high-rate charging/discharging performance and an excellent charging/discharging cycle performance and having a high energy density, and a nonaqueous electrolyte secondary cell exhibiting an excellent high-rate charging/discharging performance and an excellent charging/discharging cycle performance and having a high energy density. The main component of the positive electrode active material is a Li-Mn-Ni composite oxide, and the positive electrode active material is characterized in that the specific surface of the Li-Mn-Ni composite oxide measured by the BET method is 0.3 m^2/g or above and 1.5 m^2/g or below. The nonaqueous electrolyte secondary cell comprises such a positive electrode active material.

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(57) 要約:

高率充放電性能及び充放電サイクル性能に優れる高エネルギー密度の非水電解質二次電池を得ることのできる正極活物質、および、高率充放電性能及び充放電サイクル性能に優れる高エネルギー密度の非水電解質二次電池を提供する。

Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物を主成分とする正極活物質であって、前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物のＢＥＴ法による比表面積が０．３m^2／ｇ以上１．５m^2／ｇ以下であることを特徴とする正極活物質およびこれを用いた非水電解質二次電池。

明 細 書

正極活物質およびこれを用いた非水電解質二次電池

＜技術分野＞

本発明は、正極活物質およびこれを用いた非水電解質二次電池に関する。

＜背景技術＞

リチウム二次電池等の非水電解質二次電池は高いエネルギー密度を示し、高電圧であることから小型携帯端末や移動体通信装置などへの電源として広く使用されている。リチウム二次電池用正極活物質には、リチウムの挿入・脱離の繰り返しによっても結晶構造が安定で、かつ電気化学的作動容量が大きいことが要求される。作動電圧が４Ｖ付近のものとしては、層状構造のリチウムコバルト酸化物やリチウムニッケル酸化物、又はスピネル構造を持つリチウムマンガン酸化物等を基本構成とするリチウム含有遷移金属酸化物が知られている。

現在、４Ｖ級の作動電位を有する非水電解質二次電池の正極活物質として、$LiCoO_2$、$LiNiO_2$、$LiMnO_2$、$LiMn_2O_4$等のリチウムと遷移金属との複合酸化物が従来より知られている。なかでも、高エネルギー密度を期待できるα－$NaFeO_2$構造を有する正極活物質の中で、$LiCoO_2$等で表されるリチウムコバルト複合酸化物は民生用のリチウムイオン電池などに広く用いられているが、コバルトが希少金属であり、価格が高いといった問題があった。また、$LiNiO_2$等で表されるリチウムニッケル複合酸化物は高温での安定性に欠けるため、安全性の確保が難しいことなどから実用化には至っていない。また、$LiMn_2O_4$等で表されるスピネル構造を有するリチウムマンガン酸化物は、安価で、安全性にも優れた正極活物質であるが、リチウムコバルト複合酸化物に比べて重量当たりのエネルギー密度が７０％程度にとどまり、一部で実用化はされているものの、広く民生用途で使用されるには至っていない。

一方、$LiMnO_2$は、原理的に高い容量が期待でき、安全性にも優れるため、広く検討されてきた。前記$LiMnO_2$は、ジグザグ層状構造であるβ－NaMn

O_2型の斜方晶系構造、及び、層状岩塩構造であるα－$NaFeO_2$型の単斜晶系構造が知られている。

前記斜方晶形構造の$LiMnO_2$は、前記$LiMn_2O_4$よりも高い容量を期待できるが、充放電を繰り返すと、徐々にスピネル相への転位が生じることから、充放電サイクルに対する安定性に劣るといった問題点があった。また、前記単斜晶構造の$LiMnO_2$は、高率充放電性能が充分でなく、充放電サイクルに伴う容量低下も大きいことが、例えば、Chiang, Y-M.; Sadoway, D.R.; Jang, Y-I.; Huang, B.; Wang, H.High Capacity, Temperature-Stable Lithium Aluminium Manganese Oxide Cathodes for Rechargeable Batteries. Electrochem. Solid-State Lett.2(3), 1999, 107-110.に報告されている。

これらの問題を解決するため、特開２００１－２３６１７号公報では、$LiMnO_2$のMnをAl、Fe、Co、Ni、Mg又はCrで$1-y$（$0.5 \leqq y \leqq 1$）量置換し、且つ、正極と負極との間に６０～１００℃にて４．０Ｖ～４．８Ｖの電圧を印可して結晶構造の変化を加速し、高率充放電特性を改善する技術が開示されている。しかしながら、これらの技術を用いてもなお、高率充放電特性は十分ではなかった。

更に、前記リチウムマンガン酸化物は、その使用に当たって克服すべき技術課題が多い。特に高温時におけるサイクル性能や保存性能が劣るといった問題があった。

また、$LiNiO_2$のNiの一部をMnで置換した構造として、空間群Ｒ３／ｍの結晶構造を有する$LiNi_{1-\alpha}Mn_\alpha O_2$を考えたとき、MnによるNiサイトへの置換を確実にするためには、８００℃以上の焼成が必要である。ところが、このような高温においては、結晶中のLiが入るべきサイトにNiやMnが入り込んで結晶構造を乱してしまい、容量やサイクル性能が低下してしまうという問題点があった。特開平８－１７１９１０号公報では、前記αの値を０．０５～０．３０とし、６００℃～８００℃で焼成する技術を開示しているが、これらの技術を用いてもなお、サイクル性能は十分ではなかった。

上記の問題を解決手段として$LiNiO_2$のNiの一部をMnとCoで置換した$LiMn_aNi_bCo_cO_2$の電気化学特性に係わる技術についても公知となって

いる。例えば、特許第３２４４３１４号報には、ａ，ｂ，ｃについて０．０２≦ａ≦０．５、０．０２≦ｂ／（ｂ＋ｃ）≦０．９、ｂ＞０．３４、ａ＋ｂ＋ｃ＝１の領域に関するＬｉ複合酸化物の報告がなされている。しかしながら、本発明者らの検討によれば依然として充電時の熱的安定性に劣るといった問題を有している。この理由は定かではないが、該報告におけるＬｉ複合酸化物の作製法が固体同士の機械的混合を経由するためであって、後工程の焼成時においても金属元素の拡散が不完全で、局所的な相分離が生じる結果、熱安定性に劣る結果となっているものと推定される。また原料を過度に粉砕することによって得られるＬｉ複合酸化物の粒子が微細となり、これを正極として電池として用いた場合、正極が電解液と広く接触するために電解液の酸化分解などの副反応が起こり、経時劣化が起こりやすくなるといった問題も有している。

同様に、$LiMn_aNi_bCo_cO_2$組成のうち、Yoshinari Makimura, Naoaki Yabuuchi, Tsutomu Ohzuku, Yukinori Kayama, Isao Tanaka, and Hirohiko Adachi, Lithium Insertion Material of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ for Advanced Batteries; (II) Synthesis and Characterization as a Possible Alternative to $LiCoO_2$, The 42th Battery Synposium in Japan, 2I18, 2I19(2001)には$LiCo_{0.33}Ni_{0.33}Mn_{0.33}O_2$組成に関する報告がなされている。このＬｉ複合酸化物は、ＭｎとＮｉとＣｏの水溶液にアルカリを添加して沈殿させた共沈化合物と、Ｌｉ化合物とを混合後、熱処理することで作製される。

しかしながら、該報告には得られたＬｉ複合酸化物に関する物性の規定がなされていないといった問題があった。この種のＬｉ複合酸化物の格子体積は、充電によって収縮し、放電によって拡大するため、放電時における活物質へのＬｉの取込速度は、充電時におけるＬｉの引抜速度に比べて著しく小さい。従って、活物質と電解液との接触界面状態といった、正極へのＬｉの取込速度に強い影響を与える因子に対して最大限の注意を払わなければ、充分な放電性能を持った電池を得ることができない。従って、本活物質を正極に用いた電池を実用化するにあたっては、前記因子を決定する活物質の物性を規定することは必須の要件である。

なお、空間群の表記について、本来「Ｒ３ｍ」の数字「３」上にバー（横線）

を付して表記すべきところ、本明細書内においては便宜上「Ｒ３／ｍ」との表記をもって同一の意味を表すものとした。

本発明は、上記問題点を解決するためになされたものであって、高率充放電性能及び充放電サイクル性能に優れ、高い安全性を有する高エネルギー密度の非水電解質二次電池を得ることのできる正極活物質、および、高率充放電性能及び充放電サイクル性能に優れる高エネルギー密度の非水電解質二次電池を提供することを目的とする。

＜発明の開示＞

上記の課題を解決するために、本発明者らは鋭意検討の結果、特定の構造を有する正極活物質の物性を特定のものとすることにより、驚くべきことに、優れた電池特性を備える非水電解質二次電池が得られることを見出し、本発明に至った。すなわち、本発明の技術的構成およびその作用効果は以下の通りである。ただし、作用機構については推定を含んでおり、その作用機構の正否は、本発明を制限するものではない。

（１）　Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物を主成分とする正極活物質であって、前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物のＢＥＴ法による比表面積が０．３m^2／ｇ以上１．５m^2／ｇ以下であることを特徴とする正極活物質。

（２）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物であることを特徴とする前記（１）に記載の正極活物質。

（３）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が異種元素で置換され、次の一般式；

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

（但し、Ｍは前記異種元素　；

ｘ＝０．００１～０．１　；　ｘ´＝０．００１～０．１　；

ｙ＝０～０．１　；　ｙ´＝０～０．１　；

ｘ＋ｘ´＋ｙ＋ｙ´≦０．４　；　０≦ｚ≦１）

で示される組成の複合酸化物であることを特徴とする前記（１）に記載の正極活物質。

（４）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が異種元素で置換され、次の一般式；

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

（但し、Ｍは前記異種元素　；

ｘ＝０．０１～０．１　；　ｘ´＝０．０１～０．１　；

ｙ＝０～０．１　；　ｙ´＝０～０．１　；

ｘ＋ｘ´＋ｙ＋ｙ´≦０．２　；　０≦ｚ≦１）

で示される組成の複合酸化物であることを特徴とする前記（１）に記載の正極活物質。

（５）　前記異種元素ＭがＢ，Ｍｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｏ，Ｃｕ及びＺｎから構成される群から選ばれる１種以上であることを特徴とする前記（３）または（４）に記載の正極活物質。

（６）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が、異種元素並びにホウ素で置換され、次の一般式；

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

（但し、Ｍ’は前記異種元素　；

ｒ＝０．００１～０．１　；　ｒ´＝０．００１～０．１　；

ｓ＝０～０．１　；　ｓ´＝０～０．１　；

ｒ＋ｒ´＋ｓ＋ｓ´＋ｗ＋ｗ´≦０．４　；

ｗ＋ｗ´＝０．０００５～０．０１　；　０≦ｔ≦１）

で示される組成の複合酸化物であることを特徴とする前記（１）に記載の正極活物質。

（７）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が、異種元素並びにホウ素で置換され、次の一般式；

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

（但し、M'は前記異種元素　；

$r=0.01\sim0.1$　；　$r'=0.01\sim0.1$　；

$s=0\sim0.1$　；　$s'=0\sim0.1$　；

$r+r'+s+s'+w+w'\leqq0.2$　；

$w+w'=0.0005\sim0.01$　；　$0\leqq t\leqq1$）

で示される組成の複合酸化物であることを特徴とする前記（１）に記載の正極活物質。

（８）　前記異種元素M'がＭｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｏ，Ｃｕ及びＺｎから構成される群から選ばれる１種以上であることを特徴とする前記（６）または（７）に記載の正極活物質。

（９）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$Li[Mn_cNi_dCo_eLi_aM''_b]O_2$（M"はＭｎ、Ｎｉ、Ｃｏ、Ｌｉ以外の元素、$d\leqq c+e+a+b$、$c+d+e+a+b=1$、$0\leqq a\leqq0.05$、$0\leqq b\leqq0.05$、$0.2\leqq c\leqq0.5$、$0.02\leqq e\leqq0.4$）で表される複合酸化物であることを特徴とする前記（１）に記載の正極活物質。

（１０）　前記M"が、Ｂ，Ｍｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｕ及びＺｎからなる群から選ばれる少なくとも１種の元素であることを特徴とする前記（９）に記載の正極活物質。

（１１）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、ＣｕＫα線を使用した粉末エックス線回折図の$2\theta=18.6\pm1°$、$36.6\pm1°$、$37.8\pm1°$、$38.2\pm1°$、$44.3\pm1°$、$48.4\pm1°$、$58.4\pm1°$、$64.2\pm1°$、$64.8\pm1°$、$68.8\pm1°$にピークを有する層状結晶構造であることを特徴とする前記（１）～（１０）のいずれかに記載の正極活物質。

（１２）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、ＣｕＫα線を使用した粉末エックス線回折図の、$2\theta=18.6\pm1°$における回折ピークに対する$2\theta=44.1\pm1°$における回折ピークの相対強度比が０．６以上１．１以下であることを特徴とする前記（１）～（１１）のいずれかに記載の正極活物質。

（１３）　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、ＣｕＫα線を使用した粉末エックス線回折図の、$2\theta=18.6\pm1°$における回折ピークの半値幅が０．１

3°以上0．20°以下であり、かつ、2θ＝44．1±1°における回折ピークの半値幅が0．10°以上0．17°以下であることを特徴とする前記（1）～（12）のいずれかに記載の正極活物質。

（14） 前記Li－Mn－Ni系複合酸化物の粒径が3μm以上20μm以下である前記（1）～（13）のいずれかに記載の正極活物質。

（15） 前記（1）～（14）のいずれかに記載の正極活物質を用いた非水電解質二次電池。

本発明者らは、高容量が期待できる$LiMnO_2$に着目し、次に、Mnを置換する元素として、Mnに対して固溶が容易で、4V付近を中心とした作動電位を示すことが期待できるNiを選択した。その結果、置換量を50%とした$LiMn_{0.5}Ni_{0.5}O_2$では、従来のリチウムイオン電池との互換性に優れた4．3V～3．0Vという作動電位が得られること、及び、140mAh／gという高い放電容量が得られることを確認した。しかしながら、充放電サイクル性能については充分ではなかった。これは、充放電の繰り返しに伴って、正極活物質からMnが溶出し、これが電極界面抵抗の増加を導いているためと推察された。

そこで、本発明者らは、種々の物性を有する$LiMn_{0.5}Ni_{0.5}O_2$、および、$LiMn_{0.5}Ni_{0.5}O_2$を構成する元素のうちNi及びMnの一部を他の異種元素で置換したもの（以下、これらをまとめて、Li－Mn－Ni系複合酸化物ともいう）について、充放電サイクル性能との関係を鋭意検討したところ、比表面積の値を特定の範囲とすることにより、驚くべきことに、極めて安定した充放電サイクル性能が得られることがわかった。即ち、前記比表面積の値を1．5m^2／g以下とすることにより、優れた充放電サイクル性能が得られることがわかった。

この作用効果については、必ずしも明らかではないが、比表面積が減少したことで、正極活物質であるLi－Mn－Ni系複合酸化物が電解質に触れる面積が減少したため、電解液の酸化分解が抑制されたことに加え、前記正極活物質の粒子表面にわずかに吸着した水分が比表面積の減少に伴い減少したため、水分に起因する電池内でのフッ酸（HF）の発生量を低下させ、これらの酸によるMnの溶解反応が起こりにくくなったものと考えられる。

さらに、前記比表面積の値を０．３m^2／ｇ以上とすることにより、２Ｉｔ（０．５時間率）といった高率放電を行っても、高い放電容量を維持することが認められた。

また、本発明者らは、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の中でも、$LiMn_{0.5}Ni_{0.5}O_2$を構成する元素のうち、Ｎｉ及びＭｎの一部を他の異種元素で置換したものについて鋭意検討したところ、驚くべきことに、前記異種原子の種類を特定のものとすることで、高率放電特性をさらに大きく改善する効果があることを見いだした。

この作用効果については必ずしも明らかではないが、前記異種元素の原子半径、即ち大きさが、Ｍｎ元素やＮｉ元素の原子半径と異なるため、正極活物質を構成している層状構造に影響し、Ｌｉイオンの移動経路へ影響を及ぼし、イオン伝導を良好にする効果をもたらしたものと考えられる。また、このため、Ｍｎ、Ｎｉ以外の異種元素は、その元素の原子半径、即ち大きさが異なることから、大きさの異なる元素の存在により、充放電に伴う活物質結晶の膨張収縮歪みを緩和したものと考えられる。

さらに、特に表面組成が密接に関係することについては、Ｌｉイオンの授受が、正極活物質粒子と電解液との界面において行われることと関係しているものと考えられる。

また、本発明者らは、$LiMn_{0.5}Ni_{0.5}O_2$を合成する際の焼成条件やさらに添加するＬｉ，Ｍｎ，Ｎｉ以外の異種金属元素の種類と組成比率について鋭意検討を重ねたところ、同一組成の複合酸化物ながらも、焼成条件によって、得られる結晶の構造が大きく異なり、結晶の形態によっては充放電サイクル性能が大きく改善できることがわかった。具体的には、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物がＣｕＫα線を使用した粉末エックス線回折の2θ＝１８．６±１°、３６．６±１°、３７．８±１°、３８．２±１°、４４．３±１°、４８．４±１°、５８．４±１°、６４．２±１°、６４．８±１°、６８．８±１°にピークを有する層状結晶構造である場合、優れたサイクル性能が得られることを確認した。

この作用効果については必ずしも明らかではないが、前記粉末エックス線回折パターンを示す結晶は、歪みが少なく、結晶の構造自体が安定であるものと考え

られる。また、特にＣｏを添加した場合、更に構造を安定化させる効果があり、このため、前記結晶構造物からのリチウムの引き抜き反応が、より卑な電位で進行しやすくなった結果、充放電容量が向上したものと考えられる。

また、本発明者らは、焼成温度が８５０℃の場合と１０００℃の場合とでは、同じ成分であっても結晶構造が大きく変わり、これに伴って充放電時の電位変化曲線の形状も大きく異なっていることがわかった。特に高率放電性能に対しては、前記焼成時の温度や焼成時間がわずかに変わるだけで、影響を与える。

本発明者らは、このような事実から、焼成条件は活物質の結晶構造に影響を与えているものと考え、焼成で得られた粉末について、ＣｕＫα線を使用した粉末エックス線回折測定による回折図の２θ＝１８．６±１°における回折ピークに対する２θ＝４４．１±１°における回折ピークの相対強度に着目して鋭意検討した結果、驚くべきことに、前記相対強度が１．１以下であるリチウムマンガンニッケル複合酸化物を正極活物質として用いた場合、高率放電特性が特に改善されることがわかった。

この作用効果については、必ずしも明らかではないが、前記相対強度が１．１以下であることにより、リチウムイオンの固体内の移動が特に容易になったものと考えられる。但し、前記相対強度が０．６より小さくなった場合には、結晶の発達が悪いために、リチウムイオンの固体内の移動が阻害され、充放電サイクル性能が低下する傾向となる。このため、前記相対強度を０．６以上１．１以下とした正極活物質を用いることによって、良好な高率放電性能と良好な充放電サイクル性能とを兼ね備えた非水電解質二次電池を提供することができる。

また、２θ＝１８．６±１°と２θ＝４４．１±１°における半値幅は本発明電池に用いる正極活物質結晶の成長性や結晶子径を反映し、半値幅が大きいほど結晶子径は小さくなる関係にあると考えられるが、驚くべきことに、２θ＝１８．６±１°における回折ピークの半値幅が０．１３°～０．２０°であり、かつ、４４．１±１°における回折ピークの半値幅が０．１０°～０．１７°である場合、特に優れた高率放電特性と充放電サイクル性能が得られることが確認できた。

この作用効果については、必ずしも明らかではないが、２θ＝１８．６±１°

における回折ピークの半値幅が０．２０°以下であり、かつ、４４．１±１°における回折ピークの半値幅が０．１７°以下である場合には、結晶中のＬｉイオン移動が容易となり、高率放電特性については改善されるものの、結晶の安定性が悪くなるために、充放電サイクル性能が低下するものと考えられる。このため、2θ＝１８．６±１°における回折ピークの半値幅が０．１３°以上であり、かつ、４４．１±１°における回折ピークの半値幅が０．１０°以上である場合、適度な結晶中のＬｉイオン移動と十分な結晶の安定性とが得られるため、優れた高率放電特性と充放電サイクル性能を合わせ持つことが可能になる。

＜図面の簡単な説明＞

図１は、本発明に用いた正極活物質のエックス線光電子分光法（ＸＰＳ）による分析結果を示す図であり、図２は、実施例および比較例の電池の一部断面図であり、図３は、実施例１－１の正極活物質のエックス線回折図であり、図４は、実施例１－１０の正極活物質のエックス線回折図であり、図５は、実施例４－１の正極活物質のエックス線回折図であり、図６は、実施例１－１の電池の放電性能を示す図であり、図７は、実施例１－１０の電池の放電性能を示す図であり、図８は、実施例４－１の電池の放電性能を示す図である。

なお、図中の符号、１は安全弁、２は蓋、３はレーザー溶接部、４は負極端子、５は正極端子、６はガスケット、７は正極板、８はセパレータ、９は負極板、１０は電槽である。

＜発明を実施するための最良の形態＞

以下に、本発明の実施の形態を例示するが、本発明は、以下の実施の形態に限定されるものではない。

本発明に係る正極活物質は、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物を主成分とする正極活物質であって、前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物のＢＥＴ法による比表面積（以下、単に比表面積ともいう）が０．３m^2／ｇ以上１．５m^2／ｇ以下であることを特徴としている。前記したように、比表面積が１．５m^2／ｇ以下である

ことによって、充放電サイクル性能に優れた非水電解質二次電池（以下、単に電池ともいう）を得ることができ、比表面積が０．３m^2／ｇ以上であることによって、高率充放電性能に優れた電池を得ることができる。

ここで、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物とは、構成元素として、少なくとも、リチウム（Ｌｉ）、マンガン（Ｍｎ）、ニッケル（Ｎｉ）、酸素（Ｏ）を有する複合酸化物のことをいう。

以下に、本発明におけるＬｉ－Ｍｎ－Ｎｉ系複合酸化物の好適な形態を説明する。ただし、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、以下に例示する形態に限定されない。

Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の第一実施形態は、$LiMn_{0.5}Ni_{0.5}O_2$で表わされる複合酸化物である。

Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の第二実施形態の１は、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が異種元素で置換され、次の一般式；

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

（但し、Ｍは前記異種元素　；

$x=0.001\sim0.1$　；　$x'=0.001\sim0.1$　；

$y=0\sim0.1$　；　$y'=0\sim0.1$　；

$x+x'+y+y'\leqq0.4$　；　$0\leqq z\leqq1$）

で示される組成の複合酸化物である。

$x+x'+y+y'\leqq0.4$であることによって、充放電の繰り返しによっても複合酸化物の結晶構造が安定であり、これにより、充放電サイクル性能に優れる。

Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の第二実施形態の２は、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が異種元素で置換され、次

の一般式；

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

（但し、Mは前記異種元素　；

x＝0．01～0．1　；　x′＝0．01～0．1　；

y＝0～0．1　；　y′＝0～0．1　；

x＋x′＋y＋y′≦0．2　；　0≦z≦1）

で示される組成の複合酸化物である。

x＋x′＋y＋y′≦0．2であることによって、充放電の繰り返しによっても複合酸化物の結晶構造が特に安定であり、これにより、より充放電サイクル性能に優れる。

前記異種元素Mは、Mn、Ni及びLi以外の元素で、Mnと置換しうる元素が好ましい。例えば、B，Be，V，C，Si，P，Sc，Cu，Zn，Ga，Ge，As，Se，Sr，Mo，Pd，Ag，Cd，In，Sn，Sb，Te，Ba，Ta，W，Pb，Bi，Co，Fe，Cr，Ni，Ti，Zr，Nb，Y，Al，Na，K，Mg，Ca，Cs，La，Ce，Nd，Sm，Eu，Tb等が挙げられる。

なかでも、B，Mg，Al，Ti，V，Cr，Fe，Co，Cu及びZnのいずれかを用いると、高率放電性能に特に顕著な効果が得られるため、さらに好ましい。

ここで、Mnの置換量を示すx、yは、0＜x＋y≦0．2であり、Niの置換量を示すx′、y′は、0＜x′＋y′≦0．2である。これは、Mnの置換量x＋yとNiの置換量x′＋y′を増やすと、可逆的に使用可能なリチウム量が減少するためである。

zは、可逆的に使用可能なリチウム量を示し、Mn及びNiに対する異種元素の量が多いほど小さくなる。

ここで、式中、$Li_{y+y'}$で示される部分のリチウムについては、前記式における組成比を示すものであり、$LiMn_{0.5}Ni_{0.5}O_2$の基本骨格中におけるリチウム元素の配置状態を示すものではなく、前記基本骨格を構成する元素の一部と置換し

ているか否かを示すものでもない。

高率放電性能は、$0<x'+y'\leqq 0.2$、且つ、$0<x+y\leqq 0.2$の範囲内であれば、Mn及びNiに対する異種元素の量が多いほど向上し、x，x´は、それぞれ0．001以上が好ましく、それぞれ0．01以上が特に好ましい。

Li－Mn－Ni系複合酸化物の第三実施形態の1は、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するMn及びNiの一部が異種元素並びにホウ素で置換され、次の一般式；

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w}\cdot B_{w+w}\cdot M'_{r+r}\cdot Li_{s+s}\cdot O_2]$

（但し、M’は前記異種元素　；

$r=0.001\sim 0.1$　；　$r'=0.001\sim 0.1$　；

$s=0\sim 0.1$　；　$s'=0\sim 0.1$　；

$r+r'+s+s'+w+w'\leqq 0.4$　；

$w+w'=0.0005\sim 0.01$　；　$0\leqq t\leqq 1$）

で示される組成の複合酸化物である。

$r+r'+s+s'+w+w'\leqq 0.4$であることによって、充放電の繰り返しによっても複合酸化物の結晶構造が安定であり、これにより、充放電サイクル性能に優れる。

Li－Mn－Ni系複合酸化物の第三実施形態の2は、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するMn及びNiの一部が異種元素並びにホウ素で置換され、次の一般式；

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w}\cdot B_{w+w}\cdot M'_{r+r}\cdot Li_{s+s}\cdot O_2]$

（但し、M’は前記異種元素　；

$r=0.01\sim 0.1$　；　$r'=0.01\sim 0.1$　；

$s=0\sim 0.1$　；　$s'=0\sim 0.1$　；

$r+r'+s+s'+w+w'\leqq 0.2$　；

$w+w'=0.0005\sim 0.01$　；　$0\leqq t\leqq 1$）

で示される組成の複合酸化物である。

r＋r´＋s＋s´＋w＋w´≦０．２であることによって、充放電の繰り返しによっても複合酸化物の結晶構造が特に安定であり、これにより、より充放電サイクル性能に優れる。

なお、本明細書においては、ホウ素を含んだ正極活物質の組成表現として、

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

のように、ホウ素を置換された異種元素として表記しているが、前記ホウ素は電池の充放電によって溶解して負極上に析出することがわかっている。にもかかわらず、前記ホウ素は前記高率放電特性を改善する効果があることから、異種元素にホウ素を用いた正極活物質自身が電池内でホウ素を溶出することで、該正極活物質の結晶粒子表面に活性な面を形成する効果があり、これによって高率放電特性を改善する効果があるものと考えられる。

ここで、粒子表面の元素組成を定量する方法のひとつにエックス線光電子分光法（ＸＰＳ）により粒子をエッチングしながら測る方法がある。一例として、毎秒０．０７ｎｍの速度で粒子表面をエッチングした時のＢの濃度変化を示した（図１参照)。その結果、本例◆印の試料における粒子の場合、表面から４００秒、すなわち、２８ｎｍ程度までにほとんどのＢが集積しているのがわかる。

異種元素M’は、Ｍｎ、Ｎｉ及びＬｉ以外の元素で、Ｍｎと置換しうる元素が好ましい。例えば、Ｂｅ，Ｖ，Ｃ，Ｓｉ，Ｐ，Ｓｃ，Ｃｕ，Ｚｎ，Ｇａ，Ｇｅ，Ａｓ，Ｓｅ，Ｓｒ，Ｍｏ，Ｐｄ，Ａｇ，Ｃｄ，Ｉｎ，Ｓｎ，Ｓｂ，Ｔｅ，Ｂａ，Ｔａ，Ｗ，Ｐｂ，Ｂｉ，Ｃｏ，Ｆｅ，Ｃｒ，Ｎｉ，Ｔｉ，Ｚｒ，Ｎｂ，Ｙ，Ａｌ，Ｎａ，Ｋ，Ｍｇ，Ｃａ，Ｃｓ，Ｌａ，Ｃｅ，Ｎｄ，Ｓｍ，Ｅｕ，Ｔｂ等が挙げられる。

なかでも、Ｍｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｏ，Ｃｕ及びＺｎのいずれかを用いると、高率放電性能に特に顕著な効果が得られるため、さらに好ましい。

ここで、Ｍｎの置換量を示すｒ、ｓ、ｗは、０＜ｒ＋ｓ＋ｗ≦０．２であり、Ｎｉの置換量を示すｒ´、ｓ´、ｗ´は、０＜ｒ´＋ｓ´＋ｗ´≦０．２である

。これは、Ｍｎの置換量ｒ＋ｓ＋ｗとＮｉの置換量ｒ´＋ｓ´＋ｗ´を増やすと、可逆的に使用可能なリチウム量が減少するためである。

ｔは、可逆的に使用可能なリチウム量を示し、Ｍｎ及びＮｉに対する異種元素の量が多いほど小さくなる。

高率放電性能は、０＜ｒ´＋ｓ´＋ｗ´≦０．２、且つ、０＜ｒ＋ｓ＋ｗ≦０．２の範囲内であれば、Ｍｎ及びＮｉに対する異種元素の量が多いほど向上し、ｒ，ｒ´は、それぞれ０．００１以上が好ましく、それぞれ０．０１以上が特に好ましい。

また、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の第二実施形態および第三実施形態において、前記Ｍｎ及びＮｉの一部をリチウムや異種元素で置換する方法としては、活物質の焼成原料にあらかじめ置換する元素を添加する方法や、$LiMn_{0.5}Ni_{0.5}O_2$を焼成した後にイオン交換等により異種元素を置換する方法等が挙げられるが、これらに限定されるものではない。

Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の第四実施形態は、$Li[Mn_cNi_dCo_eLi_aM"_b]O_2$（M”はＭｎ、Ｎｉ、Ｃｏ、Ｌｉ以外の元素、ｄ≦ｃ＋ｅ＋ａ＋ｂ、ｃ＋ｄ＋ｅ＋ａ＋ｂ＝１、０≦ａ≦０．０５、０≦ｂ≦０．０５、０．２≦ｃ≦０．５、０．０２≦ｅ≦０．４）で表される複合酸化物である。ｃが０．２を下回るとサイクル性能が悪くなる傾向となり、ｃが０．５を上回るとサイクル性能が低下する傾向となるばかりでなく、原料の焼成中にLi_2MnO_3などの不純物が比較的低温から安定に生成しやすくなるので好ましくない。ｅが０．４を上回ると、充電時における熱安定性が低下する傾向となる。ａが０．０５を上回ると、放電容量が低下する傾向となる。ｂが０．０５を上回ると、放電容量が低下する傾向となる。

さらに、高率充放電特性を改善するため、構成元素の組成比を意図的に変化させて検討した結果、驚くべきことに、特定の異種元素を添加した場合、高率放電特性をさらに大きく改善する効果があることを見いだした。

前記異種元素M”は、Ｍｎ、Ｎｉ及びＬｉ以外の元素で、Ｍｎと置換しうる元

素が好ましい。例えば、Ｂ，Ｂｅ，Ｖ，Ｃ，Ｓｉ，Ｐ，Ｓｃ，Ｃｕ，Ｚｎ，Ｇａ，Ｇｅ，Ａｓ，Ｓｅ，Ｓｒ，Ｍｏ，Ｐｄ，Ａｇ，Ｃｄ，Ｉｎ，Ｓｎ，Ｓｂ，Ｔｅ，Ｂａ，Ｔａ，Ｗ，Ｐｂ，Ｂｉ，Ｆｅ，Ｃｒ，Ｎｉ，Ｔｉ，Ｚｒ，Ｎｂ，Ｙ，Ａｌ，Ｎａ，Ｋ，Ｍｇ，Ｃａ，Ｃｓ，Ｌａ，Ｃｅ，Ｎｄ，Ｓｍ，Ｅｕ，Ｔｂ等が挙げられる。

なかでも、Ｂ，Ｍｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｕ及びＺｎのいずれかを用いると、高率放電性能に特に顕著な効果が得られるため、さらに好ましい。

この作用効果については必ずしも明らかではないが、前記異種元素の大きさが、Ｍｎ元素やＮｉ元素の大きさと異なるため、正極活物質を構成している層状構造に影響し、Ｌｉイオンの移動経路へ影響を及ぼし、イオン伝導を良好にする効果をもたらしたものと考えられる。

また、Ｍｎ、Ｎｉ以外の異種元素は、その元素の原子半径、即ち大きさが異なることから、原子半径の異なる元素の存在により、充放電に伴う活物質結晶の膨張収縮歪みを緩和したものと考えられる。

また、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の第四実施形態において、前記異種元素を前記複合酸化物に取り込む方法としては、焼成原料にあらかじめ置換する元素を添加する方法や、焼成した後にイオン交換等により異種元素を置換する方法等が挙げられるが、これらに限定されるものではない。

以上に、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の各実施形態を例示したが、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、ＣｕＫα線を使用した粉末エックス線回折図の２θ＝１８．６±１°、３６．６±１°、３７．８±１°、３８．２±１°、４４．３±１°、４８．４±１°、５８．４±１°、６４．２±１°、６４．８±１°、６８．８±１°にピークを有しており、これにより優れたサイクル性能が得られる。

また、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、前記したように、ＣｕＫα線を使用した粉末エックス線回折図において、２θ＝１８．６±１°と２θ＝４４．１±１°とに回折ピークを有し、２θ＝１８．６±１°における回折ピークに対する

$2\theta = 44.1 \pm 1°$ における回折ピークの相対強度比が０．６～１．１であるものが好ましく、また、$2\theta = 18.6 \pm 1°$ における回折ピークの半値幅が０．１３°～０．２０°であり、$2\theta = 44.1 \pm 1°$ における回折ピークの半値幅が０．１０°～０．１７°であるものが好ましい。

また、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の粒子径は小さいほど比表面積が増えるため出力特性は出やすくなるが、その他の性能、特に保存性能の低下を防ぐため、また電極作製時の塗工性を考慮して、平均粒径（D_{50}）＝３μｍ～３０μｍが好ましく、特に５μｍ～２０μｍが好ましい。この範囲内であれば、電池の保存性能や充放電サイクル性能には大きく影響を与えるものではなく、特に制限されるものではない。これは、前記粒径は結晶の１次粒子の粒径を示すものでなく、２次粒子の粒径を示すものであるためである。参考までに、以下の実施例に用いた正極活物質の平均粒径は全て９～２０μｍである。

次に、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の好適な製造方法を例示する。

Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、９００℃以上の温度で焼成する熱履歴を有することが好ましい。より具体的には、「少なくともＬｉ成分とＭｎ成分とＮｉ成分とを含有するＬｉ－Ｍｎ－Ｎｉ系複合酸化物前駆体」を９００℃以上の温度で焼成してＬｉ－Ｍｎ－Ｎｉ系複合酸化物を製造することが好ましい。ここで、焼成温度は、９００℃～１１００℃が好ましく、９５０℃～１０２５℃が特に好ましい。

焼成温度が９００℃を下回ると、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の比表面積を１．５m^2／ｇ以下としにくく、サイクル性能が劣った電池が得られやすい。

一方、焼成温度が１１００℃を上回ると、Ｌｉの揮発によって目標とする組成の複合酸化物が得られにくいなどの作製上の問題や、粒子の高密度化によって電池性能が低下するという問題が生じやすい。これは、１１００℃を上回ると、１次粒子成長速度が増加し、複合酸化物の結晶粒子が大きくなりすぎることに起因しているが、それに加えて、局所的にＬｉ欠損量が増大して、構造的に不安定となっていることも原因ではないかと考えられる。

焼成時間は、３時間～５０時間が好ましい。焼成時間が５０時間を超えると、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の比表面積を０．３m^2／ｇ以上としにくく、高率充放電性能が劣った電池が得られやすい。焼成時間が３時間より少ないと、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の比表面積を１．５m^2／ｇ以下としにくく、サイクル性能が劣った電池が得られやすい。

以上に、焼成温度と焼成時間について好ましい範囲を記載したが、得られる複合酸化物の比表面積が、本発明で規定する範囲となるように適宜選択される。

Ｌｉ－Ｍｎ－Ｎｉ複合酸化物前駆体は、「マンガン（Ｍｎ）化合物とニッケル（Ｎｉ）化合物とが水に溶解された水溶液、または、Ｍｎ化合物とＮｉ化合物と“異種元素を有する化合物”（前記した異種元素Ｍ，Ｍ’，Ｍ”を含有する化合物であり、以下、［Ｍ］化合物とも表記する）とが水に溶解された水溶液に、アルカリ化合物を添加して、Ｍｎ－Ｎｉ複合共沈物、または、Ｍｎ－Ｎｉ－［Ｍ］複合共沈物を沈殿させる共沈工程」を経由して好適に製造される。

ここで、Ｎｉ化合物としては、水酸化ニッケル、炭酸ニッケル、硫酸ニッケル、硝酸ニッケル等を、Ｍｎ化合物としては、酸化マンガン、炭酸マンガン、硫酸マンガン、硝酸マンガン等を好適に挙げることができる。

［Ｍ］化合物としては、異種元素がＢである場合、ホウ酸等を、異種元素がＶである場合、酸化バナジウム等を、異種元素がＡｌである場合、硝酸アルミニウム等を、異種元素がＭｇである場合、硝酸マグネシウム等を、異種元素がＣｏである場合、水酸化コバルト、炭酸コバルト、酸化コバルト、硫酸コバルト、硝酸コバルト等を、異種元素がＣｒである場合、硝酸クロム等を、異種元素がＴｉである場合、酸化チタン等を、異種元素がＦｅである場合、硫酸鉄、硝酸鉄等を、異種元素がＣｕである場合、硫酸銅、硝酸銅等を、異種元素がＺｎである場合、硫酸亜鉛、硝酸亜鉛等を、それぞれ挙げることができる。

アルカリ化合物としては、水酸化アンモニウム、水酸化ナトリウム等を挙げることができる。また、アルカリ化合物は、水溶液の形態として添加されるのが好ましい。

以上に説明した共沈工程を経由して得られたＭｎ－Ｎｉ複合共沈物またはＭｎ－Ｎｉ－［Ｍ］複合共沈物（以下、これらをまとめて、単に“複合共沈物”ともいう）とリチウム化合物との混合物をＬｉ－Ｍｎ－Ｎｉ系複合酸化物前駆体とし、このＬｉ－Ｍｎ－Ｎｉ系複合酸化物前駆体を前記した焼成条件に基づいて焼成することによって、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物を好適に製造できる。

ここで、Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物前駆体は、複合共沈物とリチウム化合物の水溶液から水を蒸発させて乾燥させて得られた混合物を好適に例示できる。

Ｌｉ化合物としては、水酸化リチウム、炭酸リチウム等を挙げることができる。

本発明の正極活物質は、主成分である前記したＬｉ－Ｍｎ－Ｎｉ系複合酸化物に加え、他の化合物を混合して用いてもよく、例えば、他のリチウム含有遷移金属酸化物などの１種以上を混合して用いると、高いサイクル性能が得られることがある。

その他のリチウム含有遷移金属酸化物としては、一般式Li_xMX_2，$Li_xMN_yX_2$（Ｍ、ＮはＩからVIII族の金属、Ｘは酸素、硫黄などのカルコゲン化合物を示す。）であり、例えば$Li_yCo_{1-x}M_xO_2$、$Li_yMn_{2-x}M_xO_4$（Ｍは、ＩからVIII族の金属（例えは、Ｌｉ，Ｃａ，Ｃｒ，Ｎｉ，Ｆｅ，Ｃｏの１種類以上の元素）等が挙げられる。該リチウム含有遷移金属酸化物の異種元素置換量を示すｘ値については置換できる最大量まで有効であるが、好ましくは放電容量の点から０≦ｘ≦１である。また、リチウム量を示すｙ値についてはリチウムを可逆的に利用しうる最大量が有効であり、好ましくは放電容量の点から０≦ｙ≦１である。）が挙げられるが、これらに限定されるものではない。

さらに、他の化合物としては、ＣｕＯ，Cu_2O，Ag_2O，ＣｕＳ，$CuSO_4$等のＩ族金属化合物、TiS_2，SiO_2，ＳｎＯ等のIV族金属化合物、V_2O_5，V_6O_{12}，VO_x，Nb_2O_5，Bi_2O_3，Sb_2O_3等のＶ族金属化合物、CrO_3，Cr_2O_3，MoO_3，MoS_2，WO_3，SeO_2等のVI族金属化合物、MnO_2，Mn_2O_3等のVII族金属化合物、Fe_2O_3，ＦｅＯ，Fe_3O_4，Ni_2O_3，ＮｉＯ，CoO_3，ＣｏＯ等のVIII族金属化合物等で表される、例えばリチウム－コバルト系複

合酸化物やリチウムーマンガン系複合酸化物等の金属化合物、さらに、ジスルフィド，ポリピロール，ポリアニリン，ポリパラフェニレン，ポリアセチレン，ポリアセン系材料等の導電性高分子化合物、擬グラファイト構造炭素質材料等が挙げられるが、これらに限定されるものではない。

正極活物質として、前記したＬｉ－Ｍｎ－Ｎｉ系複合酸化物以外に、前掲の他の化合物を併用する場合、他の化合物の使用割合は、本発明の効果を損なわない程度であれば限定されるものではないが、その他の成分は全正極活物質中、通常１重量％～５０重量％、好ましくは５重量％～３０重量％である。

次に、本発明の非水電解質二次電池について説明する。本発明の非水電解質二次電池（以下、単に電池ともいう）は、本発明の正極活物質を用いた電池であり、一般的に、少なくとも、本発明の正極活物質を主要構成成分とする正極と、負極材料を主要構成成分とする負極と、電解質塩が非水溶媒に含有された非水電解質とから構成され、通常、正極と負極との間に、セパレータが設けられる。

非水電解質は、一般にリチウム電池等への使用が提案されているものが使用可能である。非水溶媒としては、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、クロロエチレンカーボネート、ビニレンカーボネート等の環状炭酸エステル類；γ－ブチロラクトン、γ－バレロラクトン等の環状エステル類；ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート等の鎖状カーボネート類；ギ酸メチル、酢酸メチル、酪酸メチル等の鎖状エステル類；テトラヒドロフランまたはその誘導体；１，３－ジオキサン、１，４－ジオキサン、１，２－ジメトキシエタン、１，４－ジブトキシエタン、メチルジグライム等のエーテル類；アセトニトリル、ベンゾニトリル等のニトリル類；ジオキソランまたはその誘導体；エチレンスルフィド、スルホラン、スルトンまたはその誘導体等の単独またはそれら２種以上の混合物等を挙げることができるが、これらに限定されるものではない。

電解質塩としては、例えば、$LiClO_4$，$LiBF_4$，$LiAsF_6$，$LiPF_6$，ＬｉＳＣＮ，ＬｉＢｒ，ＬｉＩ，Li_2SO_4，$Li_2B_{10}Cl_{10}$，$NaClO_4$，Ｎ

aI，NaSCN，NaBr，$KClO_4$，KSCN等のリチウム（Li）、ナトリウム（Na）またはカリウム（K）の1種を含む無機イオン塩、$LiCF_3SO_3$，$LiN(CF_3SO_2)_2$，$LiN(C_2F_5SO_2)_2$，$LiN(CF_3SO_2)(C_4F_9SO_2)$，$LiC(CF_3SO_2)_3$，$LiC(C_2F_5SO_2)_3$，$(CH_3)_4NBF_4$，$(CH_3)_4NBr$，$(C_2H_5)_4NClO_4$，$(C_2H_5)_4NI$，$(C_3H_7)_4NBr$，$(n-C_4H_9)_4NClO_4$，$(n-C_4H_9)_4NI$，$(C_2H_5)_4N$－maleate，$(C_2H_5)_4N$－benzoate，$(C_2H_5)_4N$－phtalate、ステアリルスルホン酸リチウム、オクチルスルホン酸リチウム、ドデシルベンゼンスルホン酸リチウム等の有機イオン塩等が挙げられ、これらのイオン性化合物を単独、あるいは2種類以上混合して用いることが可能である。

さらに、$LiBF_4$と$LiN(C_2F_5SO_2)_2$のようなパーフルオロアルキル基を有するリチウム塩とを混合して用いることにより、さらに非水電解質の粘度を下げることができるので、低温特性をさらに高めることができ、より望ましい。

非水電解質における電解質塩の濃度としては、高い電池特性を有する電池を確実に得るために、0．1mol／l～5mol／lが好ましく、さらに好ましくは、1mol／l～2．5mol／lである。

本発明の電池の正極には本発明によるLi－Mn－Ni系複合酸化物で構成された電極が、負極にはグラファイトで構成された電極が好適に使用される。

正極は、本発明による複合酸化物を導電剤および結着剤、さらに必要に応じてフィラーと混練して正極合剤とした後、この正極合剤を集電体としての箔やラス板等に塗布、または圧着して50℃～250℃程度の温度で、2時間程度加熱処理することにより作製される。

負極材料としては、リチウム金属、リチウム合金（リチウムーアルミニウム，リチウムー鉛，リチウムースズ，リチウムーアルミニウムースズ，リチウムーガリウム，およびウッド合金等のリチウム金属含有合金）の他、リチウムを吸蔵・放出可能な合金、炭素材料（例えばグラファイト、ハードカーボン、低温焼成炭素、非晶質カーボン等）等が挙げられる。これらの中でもグラファイトは、金属リチウムに極めて近い作動電位を有するので電解質塩としてリチウム塩を採用し

た場合に自己放電を少なくでき、かつ充放電における不可逆容量を少なくできるので、負極材料として好ましい。例えば、人造黒鉛、天然黒鉛が好ましい。特に，負極活物質粒子表面を不定形炭素等で修飾してあるグラファイトは、充電中のガス発生が少ないことから望ましい。

以下に、好適に用いることのできるグラファイトのエックス線回折等による分析結果を示す；

格子面間隔（d_{002}） ０．３３３～０．３５０ｎｍ

ａ軸方向の結晶子の大きさＬａ ２０ｎｍ 以上

ｃ軸方向の結晶子の大きさＬｃ ２０ｎｍ 以上

真密度 ２．００～２．２５ｇ／cm^3

また、グラファイトに、スズ酸化物，ケイ素酸化物等の金属酸化物、リン、ホウ素、アモルファスカーボン等を添加して改質を行うことも可能である。特に、グラファイトの表面を上記の方法によって改質することで、電解質の分解を抑制し電池特性を高めることが可能であり望ましい。さらに、グラファイトに対して、リチウム金属、リチウムーアルミニウム，リチウムー鉛，リチウムースズ，リチウムーアルミニウムースズ，リチウムーガリウム，およびウッド合金等のリチウム金属含有合金等を併用することや、あらかじめ電気化学的に還元することによってリチウムが挿入されたグラファイト等も負極活物質として使用可能である。

正極活物質の粉体及び負極材料の粉体は、平均粒子サイズ１００μｍ以下であることが望ましい。特に、正極活物質の粉体は、非水電解質電池の高出力特性を向上する目的で１０μｍ以下であることが望ましい。粉体を所定の形状で得るためには粉砕機や分級機が用いられる。例えば、乳鉢、ボールミル、サンドミル、振動ボールミル、遊星ボールミル、ジェットミル、カウンタージェトミル、旋回気流型ジェットミルや篩等が用いられる。粉砕時には水、あるいはヘキサン等の有機溶剤を共存させた湿式粉砕を用いることもできる。分級方法としては、特に限定はなく、篩や風力分級機などが、乾式、湿式ともに必要に応じて用いられる。

以上、正極及び負極の主要構成成分である正極活物質および負極材料について詳述したが、前記正極及び負極には、前記主要構成成分の他に、導電剤、結着剤、増粘剤、フィラー等が、他の構成成分として含有されてもよい。

導電剤としては、電池性能に悪影響を及ぼさない電子伝導性材料であれば限定されないが、通常、天然黒鉛（鱗状黒鉛，鱗片状黒鉛，土状黒鉛等)、人造黒鉛、カーボンブラック、アセチレンブラック、ケッチェンブラック、カーボンウイスカー、炭素繊維、金属（銅，ニッケル，アルミニウム，銀，金等）粉、金属繊維、導電性セラミックス材料等の導電性材料を１種またはそれらの混合物として含ませることができる。

これらの中で、導電剤としては、電子伝導性及び塗工性の観点よりアセチレンブラックが望ましい。導電剤の添加量は、正極または負極の総重量に対して０．１重量％～５０重量％が好ましく、特に０．５重量％～３０重量％が好ましい。特にアセチレンブラックを０．１～０．５μmの超微粒子に粉砕して用いると必要炭素量を削減できるため望ましい。これらの混合方法は、物理的な混合であり、その理想とするところは均一混合である。そのため、Ｖ型混合機、Ｓ型混合機、擂かい機、ボールミル、遊星ボールミルといったような粉体混合機を乾式、あるいは湿式で混合することが可能である。

前記結着剤としては、通常、ポリテトラフルオロエチレン（ＰＴＦＥ)，ポリフッ化ビニリデン（ＰＶＤＦ)，ポリエチレン，ポリプロピレン等の熱可塑性樹脂、エチレンープロピレンージエンターポリマー（ＥＰＤＭ)，スルホン化ＥＰＤＭ，スチレンブタジエンゴム（ＳＢＲ)、フッ素ゴム等のゴム弾性を有するポリマーを１種または２種以上の混合物として用いることができる。結着剤の添加量は、正極または負極の総重量に対して１～５０重量％が好ましく、特に２～３０重量％が好ましい。

前記増粘剤としては、通常、カルボキシメチルセルロース、メチルセルロース等の多糖類等を１種または２種以上の混合物として用いることができる。また、

多糖類の様にリチウムと反応する官能基を有する増粘剤は、例えばメチル化する等してその官能基を失活させておくことが望ましい。増粘剤の添加量は、正極または負極の総重量に対して０．５～１０重量％が好ましく、特に１～２重量％が好ましい。

フィラーとしては、電池性能に悪影響を及ぼさない材料であれば何でも良い。通常、ポリプロピレン，ポリエチレン等のオレフィン系ポリマー、無定形シリカ、アルミナ、ゼオライト、ガラス、炭素等が用いられる。フィラーの添加量は、正極または負極の総重量に対して添加量は３０重量％以下が好ましい。

正極および負極は、前記正極活物質あるいは負極材料に、必要に応じて導電剤や結着剤を加え、Ｎ－メチルピロリドン，トルエン等の有機溶媒に混合させた後、得られた混合液を下記に詳述する集電体の上に塗布し、乾燥することによって、好適に作製される。前記塗布方法については、例えば、アプリケーターロールなどのローラーコーティング、スクリーンコーティング、ドクターブレード方式、スピンコーティング、バーコータ等の手段を用いて任意の厚さおよび任意の形状に塗布することが望ましいが、これらに限定されるものではない。

集電体としては、構成された電池において悪影響を及ぼさない電子伝導体であれば何でもよい。例えば、正極用集電体としては、アルミニウム、チタン、ステンレス鋼、ニッケル、焼成炭素、導電性高分子、導電性ガラス等の他に、接着性、導電性および耐酸化性向上の目的で、アルミニウムや銅等の表面をカーボン、ニッケル、チタンや銀等で処理した物を用いることができる。負極用集電体としては、銅、ニッケル、鉄、ステンレス鋼、チタン、アルミニウム、焼成炭素、導電性高分子、導電性ガラス、Ａｌ－Ｃｄ合金等の他に、接着性、導電性、耐還元性の目的で、銅等の表面をカーボン、ニッケル、チタンや銀等で処理した物を用いることができる。これらの材料については表面を酸化処理することも可能である。

集電体の形状については、フォイル状の他、フィルム状、シート状、ネット状、パンチ又はエキスパンドされた物、ラス体、多孔質体、発砲体、繊維群の形成

体等が用いられる。厚さの限定は特にないが、１～５００μｍのものが用いられる。これらの集電体の中で、正極用としては、耐酸化性に優れているアルミニウム箔が、負極用としては、耐還元性および電子伝導性に優れ、安価な銅箔、ニッケル箔、鉄箔、およびそれらの一部を含む合金箔を使用することが好ましい。さらに、粗面表面粗さが０．２μｍＲａ以上の箔であることが好ましく、これにより正極活物質または負極活物質と集電体との密着性は優れたものとなる。よって、このような粗面を有することから、電解箔を使用するのが好ましい。特に、ハナ付き処理を施した電解箔は最も好ましい。さらに、これらの箔に両面塗工する場合、箔の表面粗さが同じ、またはほぼ等しいことが望まれる。

セパレータとしては、優れた高率放電特性を示す多孔膜や不織布等を、単独あるいは併用することが好ましい。セパレータを構成する材料としては、例えばポリエチレン，ポリプロピレン等に代表されるポリオレフィン系樹脂、ポリエチレンテレフタレート，ポリブチレンテレフタレート等に代表されるポリエステル系樹脂、ポリフッ化ビニリデン、フッ化ビニリデンーヘキサフルオロプロピレン共重合体、フッ化ビニリデンーパーフルオロビニルエーテル共重合体、フッ化ビニリデンーテトラフルオロエチレン共重合体、フッ化ビニリデンートリフルオロエチレン共重合体、フッ化ビニリデンーフルオロエチレン共重合体、フッ化ビニリデンーヘキサフルオロアセトン共重合体、フッ化ビニリデンーエチレン共重合体、フッ化ビニリデンープロピレン共重合体、フッ化ビニリデンートリフルオロプロピレン共重合体、フッ化ビニリデンーテトラフルオロエチレンーヘキサフルオロプロピレン共重合体、フッ化ビニリデンーエチレンーテトラフルオロエチレン共重合体等を挙げることができる。

セパレータの空孔率は強度の観点から９８体積％以下が好ましい。また、充放電特性の観点から空孔率は２０体積％以上が好ましい。

また、セパレータは、例えばアクリロニトリル、エチレンオキシド、プロピレンオキシド、メチルメタアクリレート、ビニルアセテート、ビニルピロリドン、ポリフッ化ビニリデン等のポリマーと電解質とで構成されるポリマーゲルを用いてもよい。

本発明の非水電解質を上記のようにゲル状態で用いると、漏液を防止する効果がある点で好ましい。

さらに、セパレータは、上述したような多孔膜や不織布等とポリマーゲルを併用して用いると、電解質の保液性が向上するため望ましい。即ち、ポリエチレン微孔膜の表面及び微孔壁面に厚さ数μm以下の親溶媒性ポリマーを被覆したフィルムを形成し、前記フィルムの微孔内に電解質を保持させることで、前記親溶媒性ポリマーがゲル化する。

前記親溶媒性ポリマーとしては、ポリフッ化ビニリデンの他、エチレンオキシド基やエステル基等を有するアクリレートモノマー、エポキシモノマー、イソシアナート基を有するモノマー等が架橋したポリマー等が挙げられる。該モノマーは、ラジカル開始剤を併用して加熱や紫外線（ＵＶ）を用いたり、電子線（ＥＢ）等の活性光線等を用いて架橋反応を行わせることが可能である。

前記親溶媒性ポリマーには、強度や物性制御の目的で、架橋体の形成を妨害しない範囲の物性調整剤を配合して使用することができる。前記物性調整剤の例としては、無機フィラー類｛酸化ケイ素、酸化チタン、酸化アルミニウム、酸化マグネシウム、酸化ジルコニウム、酸化亜鉛、酸化鉄などの金属酸化物、炭酸カルシウム、炭酸マグネシウムなどの金属炭酸塩｝、ポリマー類｛ポリフッ化ビニリデン、フッ化ビニリデン／ヘキサフルオロプロピレン共重合体、ポリアクリロニトリル、ポリメチルメタクリレート等｝等が挙げられる。前記物性調整剤の添加量は、架橋性モノマーに対して通常５０重量％以下、好ましくは２０重量％以下である。

前記アクリレートモノマーについて例示すると、二官能以上の不飽和モノマーが好適に挙げられ、より具体例には、２官能（メタ）アクリレート｛エチレングリコールジ（メタ）アクリレート、プロピレングリコールジ（メタ）アクリレート、アジピン酸・ジネオペンチルグリコールエステルジ（メタ）アクリレート、重合度２以上のポリエチレングリコールジ（メタ）アクリレート、重合度２以上のポリプロピレングリコールジ（メタ）アクリレート、ポリオキシエチレン／ポリオキシプロピレン共重合体のジ（メタ）アクリレート、ブタンジオールジ（メタ）アクリレート、ヘキサメチレングリコールジ（メタ）アクリレート等｝、３官

能（メタ）アクリレート｛トリメチロールプロパントリ（メタ）アクリレート、グリセリントリ（メタ）アクリレート、グリセリンのエチレンオキシド付加物のトリ（メタ）アクリレート、グリセリンのプロピレンオキシド付加物のトリ（メタ）アクリレート、グリセリンのエチレンオキシド、プロピレンオキシド付加物のトリ（メタ）アクリレート等｝、４官能以上の多官能（メタ）アクリレート｛ペンタエリスリトールテトラ（メタ）アクリレート、ジグリセリンヘキサ（メタ）アクリレート等｝が挙げられる。これらのモノマーを単独もしくは、併用して用いることができる。

前記アクリレートモノマーには、物性調整等の目的で１官能モノマーを添加することもできる。前記一官能モノマーの例としては、不飽和カルボン酸｛アクリル酸、メタクリル酸、クロトン酸、けい皮酸、ビニル安息香酸、マレイン酸、フマール酸、イタコン酸、シトラコン酸、メサコン酸、メチレンマロン酸、アコニット酸等｝、不飽和スルホン酸｛スチレンスルホン酸、アクリルアミドー２－メチルプロパンスルホン酸等｝またはそれらの塩（Ｌｉ塩、Ｎａ塩、Ｋ塩、アンモニウム塩、テトラアルキルアンモニウム塩等）、またこれらの不飽和カルボン酸をＣ１～Ｃ１８の脂肪族または脂環式アルコール、アルキレン（Ｃ２～Ｃ４）グリコール、ポリアルキレン（Ｃ２～Ｃ４）グリコール等で部分的にエステル化したもの（メチルマレート、モノヒドロキシエチルマレート、など）、およびアンモニア、１級または２級アミンで部分的にアミド化したもの（マレイン酸モノアミド、Ｎ－メチルマレイン酸モノアミド、Ｎ，Ｎ－ジエチルマレイン酸モノアミドなど）、（メタ）アクリル酸エステル［Ｃ１～Ｃ１８の脂肪族（メチル、エチル、プロピル、ブチル、２－エチルヘキシル、ステアリル等）アルコールと（メタ）アクリル酸とのエステル、またはアルキレン（Ｃ２～Ｃ４）グリコール（エチレングリコール、プロピレングリコール、１，４－ブタンジオール等）およびポリアルキレン（Ｃ２～Ｃ４）グリコール（ポリエチレングリコール、ポリプロピレングリコール）と（メタ）アクリル酸とのエステル］；（メタ）アクリルアミドまたはＮ－置換（メタ）アクリルアミド［（メタ）アクリルアミド、Ｎ－メチル（メタ）アクリルアミド、Ｎ－メチロール（メタ）アクリルアミド等］；ビニルエステルまたはアリルエステル［酢酸ビニル、酢酸アリル等］；ビニルエーテルまたはアリル

エーテル［ブチルビニルエーテル、ドデシルアリルエーテル等］；不飽和ニトリル化合物［(メタ) アクリロニトリル、クロトンニトリル等］；不飽和アルコール［(メタ) アリルアルコール等］；不飽和アミン［(メタ) アリルアミン、ジメチルアミノエチル(メタ)アクリルレート、ジエチルアミノエチル (メタ) アクリレート等］；複素環含有モノマー［Ｎ－ビニルピロリドン、ビニルピリジン等］；オレフィン系脂肪族炭化水素［エチレン、プロピレン、ブチレン、イソブチレン、ペンテン、(Ｃ６～Ｃ５０) α－オレフィン等］；オレフィン系脂環式炭化水素［シクロペンテン、シクロヘキセン、シクロヘプテン、ノルボルネン等］；オレフィン系芳香族炭化水素［スチレン、α－メチルスチレン、スチルベン等］；不飽和イミド［マレイミド等］；ハロゲン含有モノマー［塩化ビニル、塩化ビニリデン、フッ化ビニリデン、ヘキサフルオロプロピレン等］等が挙げられる。

前記エポキシモノマーについて例示すると、グリシジルエーテル類｛ビスフェノールＡジグリシジルエーテル、ビスフェノールＦジグリシジルエーテル、臭素化ビスフェノールＡジグリシジルエーテル、フェノールノボラックグリシジルエーテル、クレゾールノボラックグリシジルエーテル等｝、グリシジルエステル類｛ヘキサヒドロフタル酸グリシジルエステル、ダイマー酸グリシジルエステル等｝、グリシジルアミン類｛トリグリシジルイソシアヌレート、テトラグリシジルジアミノフェニルメタン等｝、線状脂肪族エポキサイド類｛エポキシ化ポリブタジエン、エポキシ化大豆油等｝、脂環族エポキサイド類｛３，４エポキシ－６メチルシクロヘキシルメチルカルボキシレート、３，４エポキシシクロヘキシルメチルカルボキシレート等｝等が挙げられる。これらのエポキシ樹脂は、単独もしくは硬化剤を添加して硬化させて使用することができる。

前記硬化剤の例としては、脂肪族ポリアミン類｛ジエチレントリアミン、トリエチレンテトラミン、３，９－（３－アミノプロピル）－２，４，８，１０－テトロオキサスピロ［５，５］ウンデカン等｝、芳香族ポリアミン類｛メタキシレンジアミン、ジアミノフェニルメタン等｝、ポリアミド類｛ダイマー酸ポリアミド等｝、酸無水物類｛無水フタル酸、テトラヒドロメチル無水フタル酸、ヘキサヒドロ無水フタル酸、無水トリメリット酸、無水メチルナジック酸｝、フェノール類｛フェノールノボラック等｝、ポリメルカプタン｛ポリサルファイド等｝、第三アミン

類｛トリス（ジメチルアミノメチル）フェノール、２－エチル－４－メチルイミダゾール等｝、ルイス酸錯体｛三フッ化ホウ素・エチルアミン錯体等｝等が挙げられる。

前記イソシアナート基を有するモノマーについて例示すると、トルエンジイソシアナート、ジフェニルメタンジイソシアナート、１，６－ヘキサメチレンジイソシアナート、２，２，４（２，２，４）－トリメチル－ヘキサメチレンジイソシアナート、ｐ－フェニレンジイソシアナート、４，４´－ジシクロヘキシルメタンジイソシアナート、３，３´－ジメチルジフェニル４，４´－ジイソシアナート、ジアニシジンジイソシアナート、ｍ－キシレンジイソシアナート、トリメチルキシレンジイソシアナート、イソフォロンジイソシアナート、１，５－ナフタレンジイソシアナート、ｔｒａｎｓ－１，４－シクロヘキシルジイソシアナート、リジンジイソシアナート等が挙げられる。

前記イソシアナート基を有するモノマーを架橋するにあたって、ポリオール類およびポリアミン類［２官能化合物｛水、エチレングリコール、プロピレングリコール、ジエチレングリコール、ジプロピレングリコール等｝、３官能化合物｛グリセリン、トリメチロールプロパン、１，２，６－ヘキサントリオール、トリエタノールアミン等｝、４官能化合物｛ペンタエリスリトール、エチレンジアミン、トリレンジアミン、ジフェニルメタンジアミン、テトラメチロールシクロヘキサン、メチルグルコシド等｝、５官能化合物｛２，２，６，６－テトラキス（ヒドロキシメチル）シクロヘキサノール、ジエチレントリアミンなど｝、６官能化合物｛ソルビトール、マンニトール、ズルシトール等｝、８官能化合物｛スークロース等｝］、およびポリエーテルポリオール類｛前記ポリオールまたはポリアミンのプロピレンオキサイドおよび／またはエチレンオキサイド付加物｝、ポリエステルポリオール［前記ポリオールと多塩基酸｛アジピン酸、ｏ，ｍ，ｐ－フタル酸、コハク酸、アゼライン酸、セバシン酸、リシノール酸｝との縮合物、ポリカプロラクトンポリオール｛ポリε－カプロラクトン等｝、ヒドロキシカルボン酸の重縮合物等］等、活性水素を有する化合物を併用することができる。

前記架橋反応にあたって、触媒を併用することができる。前記触媒について例示すると、有機スズ化合物類、トリアルキルホスフィン類、アミン類［モノアミ

ン類｛N，N－ジメチルシクロヘキシルアミン、トリエチルアミン等｝、環状モノアミン類｛ピリジン、N－メチルモルホリン等｝、ジアミン類｛N，N，N′，N′－テトラメチルエチレンジアミン、N，N，N′，N′－テトラメチル１，３－ブタンジアミン等｝、トリアミン類｛N，N，N′，N′－ペンタメチルジエチレントリアミン等｝、ヘキサミン類｛N，N，N′N′－テトラ（３－ジメチルアミノプロピル）－メタンジアミン等｝、環状ポリアミン類｛ジアザビシクロオクタン（ＤＡＢＣＯ）、N，N′－ジメチルピペラジン、１，２－ジメチルイミダゾール、１，８－ジアザビシクロ（５，４，０）ウンデセン－７（ＤＢＵ）等｝等、およびそれらの塩類等が挙げられる。

本発明に係る非水電解質二次電池は、電解質を、例えば、セパレータと正極と負極とを積層する前または積層した後に注液し、最終的に、外装材で封止することによって好適に作製される。また、正極と負極とがセパレータを介して積層された発電要素を巻回してなる非水電解質電池においては、電解質は、前記巻回の前後に発電要素に注液されるのが好ましい。注液法としては、常圧で注液することも可能であるが、真空含浸方法や加圧含浸方法も使用可能である。

非水電解質二次電池の外装体の材料としては、ニッケルメッキした鉄やステンレススチール、アルミニウム、金属樹脂複合フィルム等が一例として挙げられる。例えば、金属箔を樹脂フィルムで挟み込んだ構成の金属樹脂複合フィルムが好ましい。前記金属箔の具体例としては、アルミニウム、鉄、ニッケル、銅、ステンレス鋼、チタン、金、銀等、ピンホールのない箔であれば限定されないが、好ましくは軽量且つ安価なアルミニウム箔が好ましい。また、電池外部側の樹脂フィルムとしては、ポリエチレンテレフタレートフィルム，ナイロンフィルム等の突き刺し強度に優れた樹脂フィルムを、電池内部側の樹脂フィルムとしては、ポリエチレンフィルム，ナイロンフィルム等の、熱融着可能であり、かつ耐溶剤性を有するフィルムが好ましい。

非水電解質二次電池の構成については特に限定されるものではなく、正極、負極および単層又は複層のセパレータを有するコイン電池やボタン電池、さらに、正極、負極およびロール状のセパレータを有する円筒型電池、角型電池、扁平型

電池等が一例として挙げられる。

＜実施例＞

次に、前記した各実施形態における実施例および比較例を挙げて本発明を具体的に説明するが、本発明は、以下の実施例によって限定されるものではない。

［第一実施形態］

（実施例１－１）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、２θ＝１８．５８度、３６．３８度、３７．６８度、３８．０２度、４４．１０度、４８．２４度、５８．２２度、６３．９２度、６４．１０度、６４．４度及び６７．６８度付近にそれぞれ回折ピークが認められ、完全に一致しているわけではないが空間群Ｒ３／ｍに属する層状構造と思われる結晶性の高い単相が合成できていることがわかった。該粉末のエックス線回折図を図３に示す。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を粉末Ａとする。

該粉末Ａを正極活物質として用い、次のようにして図２に示す容量約１５Ａｈの角形非水電解質電池を作製した。

正極活物質である粉末Ａ、導電剤であるアセチレンブラック及び結着剤であるポリフッ化ビニリデン（ＰＶＤＦ）を重量比８５：１０：５で混合し、溶剤としてＮ－メチルピロリドンを加え、混練分散し正極塗布液を調製した。なお、前記ポリフッ化ビニリデンは固形分が溶解分散された溶解液を用い、固形分として重量換算した。前記正極塗布液を厚さ２０μｍのアルミ箔集電体の両面に塗布し、全体の厚さを２３０μｍに調整し、６．３ｍＡｈ／cm^2の容量を持つ正極シー

トを作製した。前記正極シートを幅６１ｍｍ、高さ１０７ｍｍの形状に裁断して、シートの末端に厚さ２０μｍ、幅１０ｍｍのアルミニウムリード板を取り付け、正極板７とした。

人造黒鉛（粒径６μｍ）を負極材料として用い、結着剤であるポリフッ化ビニリデン（ＰＶＤＦ）を前記負極材料に対して１０重量％加え、溶剤としてＮ－メチルピロリドンを加え、混練分散し、負極塗布液を調製した。なお、前記ポリフッ化ビニリデンは固形分が溶解分散された溶解液を用い、固形分として重量換算した。前記負極塗布液を厚さ１０μｍの銅箔集電体の両面に塗布し、全体の厚さを１８０μｍに調整し、７ｍＡｈ／ｃｍ^{2}の容量を持つ負極シートを作製した。前記負極シートを幅６５ｍｍ、高さ１１１ｍｍの形状に裁断して、シートの末端に厚さ１０μｍ、幅１０ｍｍの銅リード板を取り付け、負極板９とした。

前記正極板７及び負極板９を１５０℃で１２時間減圧乾燥した。次に、セパレータ８として、幅６５ｍｍ、高さ１１１ｍｍの袋形状に裁断したポリエチレン製微多孔膜の袋に前記正極板を挿入し、セパレータ８付き正極板７、負極板９の順でこれらを交互に積層し、４０枚のセパレータ８付き正極板７及び４１枚の負極板９からなる極群を得た。

前記極群をポリエチレン樹脂からなる絶縁フィルムに包み込み、アルミニウム製の角形電槽１０に収納し、安全弁１を有するアルミニウム製の蓋２に取り付けられた正極端子５及び負極端子４に、正極板７及び負極板９のリード板をそれぞれボルトによって接続した。なお、端子５，４はポリプロピレン樹脂からなるガスケット６を用いて前記蓋２との間を絶縁してある。

前記蓋２と電槽１０とをレーザー溶接部３においてレーザー溶接し、前記電槽１０の中に、エチレンカーボネートとジエチルカーボネートとの体積比１：１の混合溶剤に$LiPF_6$を１ｍｏｌ／ｌ溶解した電解液を６５ｇ注入し、封口した後、２５℃において、１．５Ａ、４．２Ｖ、１５時間の定電流定電圧充電を行い、１．５Ａ、終止電圧３Ｖの定電流放電を行った。このようにして、横７０ｍｍ、高さ１３０ｍｍ（端子込み高さ１３６ｍｍ）、幅２２ｍｍの角形リチウム電池を得た。この電池を実施例１－１の電池とする。

（実施例１－２）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガン－ニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガン－ニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－２の電池とする。

（実施例１－３）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガン－ニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガン－ニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０３０℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－３の電池とする。

（実施例１－４）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、

マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０６０℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－４の電池とする。

（実施例１－５）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－５の電池とする。

（実施例１－６）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、９５０℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末と

した。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－６の電池とする。

（実施例１－７）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、９６０℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－７の電池とする。

（実施例１－８）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、９８０℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結

果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は実施例（１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－８の電池とする。

（実施例１－９）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で５時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．３m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－９の電池とする。

（実施例１－１０）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で５時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．３m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。該粉末のエックス線回折図を図４に示す。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例

１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－１０の電池とする。

（実施例１－１１）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で２０時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝５μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．５m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は実施例（１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例１－１１の電池とする。

（比較例１－１）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１．９：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、９５０℃で３時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．６m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、２θ＝１８度、３７度、３９度、４５度、６１度、６５度、６７度に回折ピークが認められ、空間群Ｃ２／ｍに属する層状岩塩型の結晶が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.95}Ni_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は実施例（１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例１－１の電池とす

る。

（比較例１－２）

硝酸マンガンを含む水溶液に水酸化ナトリウム水溶液を加えて沈殿させ、１５０℃で加熱、乾燥して、マンガン化合物を得た。水酸化リチウム水溶液に前記マンガン化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、８５０℃で３時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝１０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．４m^2／ｇであった。前記粉末のＣｕＫα線によるエックス線回折測定の結果、スピネル構造を有する結晶が合成できていることがわかった。元素分析の結果、該粉末の組成は$Li_{1.05}Mn_{1.95}O_4$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例１－２の電池とする。

（比較例１－３）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で３時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝３μｍの粉末とした。ＢＥＴ法により測定した比表面積は２．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例１－３の電池とする。

（比較例１－４）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む

水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、８００℃で１５時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝５μｍの粉末とした。ＢＥＴ法により測定した比表面積は２．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例１－４の電池とする。

（比較例１－５）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で２４時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝５μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．２m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す設計容量１５Ａｈの角形リチウム電池を作製した。この電池を比較例１－５の電池とする。

（比較例１－６）

硝酸マンガン及び硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が１：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウム水溶液に前記マンガン

ーニッケル共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１１００℃で２４時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝３０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．２m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.5}Ni_{0.5}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例１－６の電池とする。

［第二実施形態］

（実施例２－１）

硝酸マンガン、硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が０．９５：０．９５の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウムに前記マンガンーニッケル共沈化合物とホウ酸を、元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｂが２：０．９５：０．９５：０．１０となるように添加し、１０００℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－１の電池とする。

（実施例２－２）

硝酸マンガン、硝酸ニッケル及び酸化バナジウムを、Ｍｎ：Ｎｉ：Ｖの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーバナジウム共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーバナジウ

ム共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}V_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－２の電池とする。

（実施例２－３）

硝酸マンガン、硝酸ニッケル及び硝酸アルミニウムを、Ｍｎ：Ｎｉ：Ａｌの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーアルミニウム共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーアルミニウム共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Al_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－３の電池とする。

（実施例２－４）

硝酸マンガン、硝酸ニッケル及び硝酸マグネシウムを、Ｍｎ：Ｎｉ：Ｍｇの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーマグネシウム共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーマグネシウム共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００

℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－４の電池とする。

（実施例２－５）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーコバルト共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Co_{0.05}O_2$であることがわかった。この粉末を粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－５の電池とする。

（実施例２－６）

硝酸マンガン、硝酸ニッケル及び硝酸クロムを、Ｍｎ：Ｎｉ：Ｃｒの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルークロム共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーマグネシウム共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。Ｂ

ＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Cr_{0.05}O_2$であることがわかった。この粉末を粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－６の電池とする。

（実施例２－７）

硝酸マンガン、硝酸ニッケル及び酸化チタンを、Ｍｎ：Ｎｉ：Ｔｉの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーチタン共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーチタン共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Ti_{0.05}O_2$であることがわかった。この粉末を粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－７の電池とする。

（実施例２－８）

硝酸マンガン、硝酸ニッケル及び硫酸鉄を、Ｍｎ：Ｎｉ：Ｆｅの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルー鉄共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルー鉄共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折

測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Fe_{0.05}O_2$であることがわかった。この粉末を粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－８の電池とする。

（実施例２－９）

硝酸マンガン、硝酸ニッケル及び硫酸銅を、Ｍｎ：Ｎｉ：Ｃｕの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルー銅共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルー銅共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Cu_{0.05}O_2$であることがわかった。この粉末を粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－９の電池とする。

（実施例２－１０）

硝酸マンガン、硝酸ニッケル及び硫酸亜鉛を、Ｍｎ：Ｎｉ：Ｚｎの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルー亜鉛共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルー亜鉛共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成

できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Zn_{0.05}O_2$であることがわかった。この粉末を粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例２－１０の電池とする。

（比較例２－１）

硝酸マンガン、硝酸ニッケル及び硝酸マグネシウムを、Ｍｎ：Ｎｉ：Ｍｇの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーマグネシウム共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーマグネシウム共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝１５μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．２m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例２－１の電池とする。

（比較例２－２）

硝酸マンガン、硝酸ニッケル及び硝酸マグネシウムを、Ｍｎ：Ｎｉ：Ｍｇの原子比が０．９５：０．９５：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーマグネシウム共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーマグネシウム共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝６μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．９m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられ

る結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例２－２の電池とする。

［第三実施形態］

（実施例３－１）

硝酸マンガン、硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が０．９５：０．９５の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウムに前記マンガンーニッケル共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｂが２．００：０．９５：０．９５：０．１となるように添加し、１０００℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。該粉末を粉末Ｂとする。元素分析の結果、該粉末Ｂの組成は$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$であることがわかった。

深さ方向分析ではＢ（ホウ素）は表面に偏析しているのが観測された（図１参照)。該粉末Ｂを正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－１の電池とする。

（実施例３－２）

硝酸マンガン、硝酸ニッケル、酸化バナジウムを、Ｍｎ：Ｎｉ：Ｖの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーバナジウム共沈化合物を得た。水酸化リチウムに前記マンガンーニッケルーバナジウム共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｖ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気

下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}V_{0.05}B_{0.001}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－２の電池とする。

（実施例３－３）

硝酸マンガン、硝酸ニッケル、硝酸アルミニウムを、Ｍｎ：Ｎｉ：Ａｌの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーアルミニウム共沈化合物を得た。水酸化リチウムに前記マンガンーニッケルーアルミニウム共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ａｌ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Al_{0.05}B_{0.001}O_2$であることがわかった。該粉末を粉末とする。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－３の電池とする。

（実施例３－４）

硝酸マンガン、硝酸ニッケル、硝酸マグネシウムを、Ｍｎ：Ｎｉ：Ｍｇの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーマグネ

シウム共沈化合物を得た。水酸化リチウム水溶液にマンガンーニッケルーマグネシウム共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｍｇ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Mg_{0.05}B_{0.001}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－４の電池とする。

（実施例３－５）

硝酸マンガン、硝酸ニッケル、硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーコバルト共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｃｏ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Co_{0.05}B_{0.001}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－５の電池とする。

（実施例３－６）

硝酸マンガン、硝酸ニッケル、硝酸クロムを、Ｍｎ：Ｎｉ：Ｃｒの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルークロム共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルークロム共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｃｒ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Cr_{0.05}B_{0.001}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－６の電池とする。

（実施例３－７）

硝酸マンガン、硝酸ニッケル、酸化チタンを、Ｍｎ：Ｎｉ：Ｔｉの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーチタン共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルーチタン共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｔｉ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Ti_{0.05}B_{0.001}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－

７の電池とする。

（実施例３－８）

硝酸マンガン、硝酸ニッケル、硫酸鉄を、Ｍｎ：Ｎｉ：Ｆｅの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルー鉄共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルー鉄共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｆｅ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Fe_{0.05}B_{0.001}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－８の電池とする。

（実施例３－９）

硝酸マンガン、硝酸ニッケル、硫酸銅を、Ｍｎ：Ｎｉ：Ｃｕの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルー銅共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルー銅共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｃｕ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Cu_{0.05}B_{0.001}$

O_2であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－９の電池とする。

（実施例３－１０）

硝酸マンガン、硝酸ニッケル、硫酸亜鉛を、Ｍｎ：Ｎｉ：Ｚｎの原子比が０．９５：０．９４８：０．１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルー亜鉛共沈化合物を得た。水酸化リチウム水溶液に前記マンガンーニッケルー亜鉛共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｚｎ：Ｂが２：０．９５：０．９４８：０．１：０．００２となるように添加し、１０００℃で１２時間、酸素雰囲気下で本焼成した後、粒子を分級してD_{50}＝１０μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.474}Zn_{0.05}B_{0.001}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例３－１０の電池とする。

（比較例３－１）

硝酸マンガン、硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が０．９５：０．９５の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウムに前記マンガンーニッケル共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｂが２．００：０．９５：０．９５：０．１となるように添加し、１０００℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．２m^2／ｇであった。該粉末のＣｕＫα線によるエッ

クス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例３－１の電池とする。

（比較例３－２）

硝酸マンガン、硝酸ニッケルを、Ｍｎ：Ｎｉの原子比が０．９５：０．９５の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケル共沈化合物を得た。水酸化リチウムに前記マンガンーニッケル共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｂが２．００：０．９５：０．９５：０．１となるように添加し、１０００℃で１２時間、酸素雰囲気下で焼成した後、粒子を分級してD_{50}＝４μｍの粉末とした。ＢＥＴ法により測定した比表面積は２．４m^2／ｇであった。該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ａと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$であることがわかった。

該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例３－２の電池とする。

［第四実施形態］

（実施例４－１）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が９：９：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥して、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝２０

μmの粉末とした。ＢＥＴ法で測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、２θ＝１８．５６度、３６．５６度、３７．７６度、３８．２４度、４４．３２度、４８．４度、５８．４度、６４．１６度、６４．８度、６８．８度に回折ピークが認められ、空間群Ｒ３ｍに属する層状構造と思われる結晶性の高い単相が合成できていることがわかった。該粉末のエックス線回折図を図５に示す。元素分析の結果、該粉末の組成は$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$であることがわかった。該粉末を粉末Ｄとする。

該粉末Ｄを正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－１の電池とする。

（実施例４－２）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が２：２：１の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝２０μmの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－２の電池とする。

（実施例４－３）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が９：９：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、

１５０℃で加熱、乾燥し、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で５時間、酸素雰囲気下で焼成した後、分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．３m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－３の電池とする。

（実施例４－４）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が９：９：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で２０時間、酸素雰囲気下で焼成した後、分級してD_{50}＝５μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．５m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－４の電池とする。

（実施例４－５）

硝酸マンガン、硝酸ニッケル、硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が１７：１７：４の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルト共沈化合物を得た。

水酸化リチウムに該共沈化合物とホウ酸を元素比Ｌｉ：Ｍｎ：Ｎｉ：Ｃｏ：Ｂが２：０．８５：０．８５：０．２：０．１となるように添加し、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}B_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－５の電池とする。

（実施例４－６）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び酸化バナジウムを、Ｍｎ：Ｎｉ：Ｃｏ：Ｖの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトーバナジウム共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}V_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－６の電池とする。

（実施例４－７）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び硝酸アルミニウムを、Ｍｎ：Ｎｉ：Ｃｏ：Ａｌの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナ

トリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトーアルミニウム共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}Al_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－７の電池とする。

（実施例４－８）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び硝酸マグネシウムを、Ｍｎ：Ｎｉ：Ｃｏ：Ｍｇの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトーマグネシウム共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}Mg_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－８の電池とする。

（実施例４－９）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び硝酸クロムを、Ｍｎ：Ｎｉ：

Ｃｏ：Ｃｒの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトークロム共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}Cr_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－９の電池とする。

（実施例４－１０）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び酸化チタンを、Ｍｎ：Ｎｉ：Ｃｏ：Ｔｉの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトーチタン共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}Ti_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－１０の電池とする。

（実施例４－１１）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び硫酸鉄を、Ｍｎ：Ｎｉ：Ｃｏ：Ｆｅの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトー鉄共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}Fe_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－１１の電池とする。

（実施例４－１２）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び硫酸銅を、Ｍｎ：Ｎｉ：Ｃｏ：Ｃｕの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトー銅共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}Cu_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－１２の電池とする。

（実施例４－１３）

硝酸マンガン、硝酸ニッケル、硝酸コバルト及び硫酸亜鉛を、Ｍｎ：Ｎｉ：Ｃｏ：Ｚｎの原子比が１７：１７：４：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルトー亜鉛共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝９μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．９m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.425}Ni_{0.425}Co_{0.1}Zn_{0.05}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を実施例４－１３の電池とする。

（比較例４－１）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が７：１１：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で１２時間、酸素雰囲気下で焼成した後、分級してD_{50}＝２０μｍの粉末とした。ＢＥＴ法により測定した比表面積は１．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.35}Ni_{0.55}Co_{0.1}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例４－１の電池とする。

（比較例４－２）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が９：９：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で２４時間、酸素雰囲気下で焼成した後、分級してD_{50}＝５μｍの粉末とした。ＢＥＴ法により測定した比表面積は０．３m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例４－２の電池とする。

（比較例４－３）

硝酸マンガン、硝酸ニッケル及び硝酸コバルトを、Ｍｎ：Ｎｉ：Ｃｏの原子比が９：９：２の割合で含む水溶液に水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱、乾燥し、マンガンーニッケルーコバルト共沈化合物を得た。水酸化リチウム水溶液に該共沈化合物を添加し、撹拌後溶媒を蒸発させて乾燥した後、１０００℃で３時間、酸素雰囲気下で焼成した後、分級してD_{50}＝５μｍの粉末とした。ＢＥＴ法により測定した比表面積は２．０m^2／ｇであった。

該粉末のＣｕＫα線によるエックス線回折測定の結果、粉末Ｄと同様な層状構造とみられる結晶性の高い単相が合成できていることがわかった。元素分析の結果、該粉末の組成は$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$であることがわかった。該粉末を正極活物質として用いたこと以外は（実施例１－１）と同様にして図２に示す容量約１５Ａｈの角形リチウム電池を作製した。この電池を比較例４－３の電池とする。

（電池性能試験）

以上の本発明電池及び比較電池を用いて、温度２５℃で高率放電性能試験を行い、引き続き、充放電サイクル性能試験を行なった。

高率放電性能試験の条件は、充電は電流７．５Ａ（０．５Ｉｔ）、４．３Ｖ、３時間の定電流定電圧充電とし、放電は電流１．５Ａ（０．１Ｉｔ）または３０Ａ（２Ｉｔ）、終止電圧３．０Ｖの定電流放電とした。

充放電サイクル性能試験の条件は、充電は電流７．５Ａ（０．５Ｉｔ）、４．３Ｖ、３時間の定電流定電圧充電とし、放電は電流７．５Ａ（０．５Ｉｔ）、終止電圧３．０Ｖの定電流放電とした。充電後及び放電後には、それぞれ１０分の休止モードを挿入した。

高率放電試験において、３０Ａの電流で放電したときの放電容量の、１．５Ａの電流で放電したときの放電容量に対する比を高率放電性能値（％）とした。充放電サイクル性能試験において、放電容量が、前記充放電サイクル性能試験を開始した初期の放電容量に対して８０％にまで低下したときのサイクル数をサイクル寿命とした。これらの性能試験の結果を表１～表４に示す。表中、“半値幅１８．６°”とは、$2\theta=18.6\pm1°$における回折ピークの半値幅を示し、“半値幅４４．１°”とは、$2\theta=44.1\pm1°$における回折ピークの半値幅を示し、“ピーク強度比”とは、$2\theta=18.6\pm1°$における回折ピークに対する$2\theta=44.1\pm1°$における回折ピークの相対強度比を示す。

表1

電池	正極活物質						電池性能			
	組成	比表面積 (g/m^2)	平均粒径 (μm)	ピーク強度比	半値幅 18.6°	半値幅 44.1°	1.5A放電容量 (mAh/g)	30A放電容量 (mAh/g)	高率放電性能値 (%)	サイクル寿命
実施例1-1	$LiMn_{0.5}Ni_{0.5}O_2$	1.0	9	1.0	0.17	0.15	140	85	60.7	500
実施例1-2	$LiMn_{0.5}Ni_{0.5}O_2$	1.0	20	0.9	0.17	0.14	140	85	60.7	500
実施例1-3	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	0.6	0.20	0.17	150	92	61.3	350
実施例1-4	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	0.6	0.17	0.15	150	93	62.0	450
実施例1-5	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	1.1	0.17	0.12	135	81	60.0	480
実施例1-6	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	1.1	0.13	0.10	135	78	57.8	520
実施例1-7	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	1.2	0.17	0.12	130	65	50.0	550
実施例1-8	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	1.0	0.12	0.10	137	62	45.3	500
実施例1-9	$LiMn_{0.5}Ni_{0.5}O_2$	0.3	20	0.9	0.18	0.15	140	84	60.0	510
実施例1-10	$LiMn_{0.5}Ni_{0.5}O_2$	0.3	9	0.9	0.17	0.15	140	84	60.0	510
実施例1-11	$LiMn_{0.5}Ni_{0.5}O_2$	1.5	5	0.9	0.17	0.15	140	85	60.7	470
比較例1-1	$LiMn_{0.95}Ni_{0.05}O_2$	0.6	20	0.6	0.20	0.17	160	50	31.3	300
比較例1-2	$Li_{1.05}Mn_{1.95}O_4$	0.4	10	0.7	0.17	0.12	118	90	76.3	350
比較例1-3	$LiMn_{0.5}Ni_{0.5}O_2$	2.0	3	0.9	0.17	0.17	140	87	62.1	250
比較例1-4	$LiMn_{0.5}Ni_{0.5}O_2$	2.0	5	0.4	0.21	0.18	110	70	63.6	250
比較例1-5	$LiMn_{0.5}Ni_{0.5}O_2$	0.2	5	0.9	0.19	0.14	140	87	62.1	250
比較例1-6	$LiMn_{0.5}Ni_{0.5}O_2$	0.2	30	0.9	0.12	0.10	120	72	60.0	480

表2

電池	正極活物質						電池性能			
	組成	比表面積 (g/m^2)	平均粒径 (μm)	ピーク強度比	半値幅 18.6°	半値幅 44.1°	1.5A放電容量 (mAh/g)	30A放電容量 (mAh/g)	高率放電性能値 (%)	サイクル寿命
実施例2-1	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	0.9	9	0.9	0.16	0.10	137	89	65.0	350
実施例2-2	$LiMn_{0.475}Ni_{0.475}V_{0.05}O_2$	0.9	9	0.9	0.17	0.17	130	87	66.9	350
実施例2-3	$LiMn_{0.475}Ni_{0.475}Al_{0.05}O_2$	0.9	9	1.0	0.16	0.11	129	89	69.0	350
実施例2-4	$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$	0.9	9	1.1	0.16	0.12	132	89	67.4	350
実施例2-5	$LiMn_{0.475}Ni_{0.475}Co_{0.05}O_2$	0.9	9	1.0	0.16	0.14	128	88	68.8	350
実施例2-6	$LiMn_{0.475}Ni_{0.475}Cr_{0.05}O_2$	0.9	9	0.9	0.17	0.17	128	84	65.6	350
実施例2-7	$LiMn_{0.475}Ni_{0.475}Ti_{0.05}O_2$	0.9	9	0.9	0.16	0.17	129	87	67.4	350
実施例2-8	$LiMn_{0.475}Ni_{0.475}Fe_{0.05}O_2$	0.9	9	0.9	0.16	0.13	128	85	66.4	350
実施例2-9	$LiMn_{0.475}Ni_{0.475}Cu_{0.05}O_2$	0.9	9	0.9	0.16	0.14	127	83	65.4	350
実施例2-10	$LiMn_{0.475}Ni_{0.475}Zn_{0.05}O_2$	0.9	9	0.9	0.17	0.13	128	84	65.6	350
比較例2-1	$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$	0.2	15	1.1	0.17	0.11	95	40	42.1	300
比較例2-2	$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$	1.9	6	1.1	0.16	0.10	130	90	69.2	150

表3

電池	正極活物質						電池性能			
	組成	比表面積 (g/m^2)	平均粒径 (μm)	ピーク強度比	半値幅 18.6°	半値幅 44.1°	1.5A放電容量 (mAh/g)	30A放電容量 (mAh/g)	高率放電性能値 (%)	サイクル寿命
実施例3-1	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	1.0	9	1.0	0.15	0.12	137	89	65.0	600
実施例3-2	$LiMn_{0.475}Ni_{0.474}V_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.14	0.11	130	90	69.2	550
実施例3-3	$LiMn_{0.475}Ni_{0.474}Al_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.13	0.11	129	92	71.3	600
実施例3-4	$LiMn_{0.475}Ni_{0.474}Mg_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.13	0.11	132	92	69.7	650
実施例3-5	$LiMn_{0.475}Ni_{0.474}Co_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.13	0.11	131	93	71.0	700
実施例3-6	$LiMn_{0.475}Ni_{0.474}Cr_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.14	0.11	128	87	68.0	650
実施例3-7	$LiMn_{0.475}Ni_{0.474}Ti_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.16	0.14	129	90	69.8	500
実施例3-8	$LiMn_{0.475}Ni_{0.474}Fe_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.16	0.14	125	86	68.8	480
実施例3-9	$LiMn_{0.475}Ni_{0.474}Cu_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.15	0.13	127	85	66.9	500
実施例3-10	$LiMn_{0.475}Ni_{0.474}Zn_{0.05}B_{0.001}O_2$	1.0	10	1.0	0.16	0.15	130	93	71.5	510
比較例3-1	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	0.2	9	1.1	0.18	0.23	110	70	63.6	470
比較例3-2	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	2.4	4	1.1	0.17	0.21	132	95	72.0	200

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表4

電池	正極活物質						電池性能			
	組成	比表面積 (g/m^2)	平均粒径 (μm)	ピーク強度比	半値幅 18.6°	半値幅 44.1°	1.5A放電容量 (mAh/g)	30A放電容量 (mAh/g)	高率放電性能値 (%)	サイクル寿命
実施例4-1	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	0.9	20	1.0	0.19	0.12	160	113	70.6	700
実施例4-2	$LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$	0.9	20	1.0	0.19	0.11	165	120	72.7	750
実施例4-3	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	0.3	20	1.0	0.15	0.14	160	112	70.0	600
実施例4-4	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	1.5	5	1.0	0.19	0.10	160	114	71.3	700
比較例4-1	$LiMn_{0.35}Ni_{0.55}Co_{0.1}O_2$	1.0	20	1.0	0.17	0.13	160	115	71.9	400
比較例4-2	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	0.3	5	1.0	0.20	0.10	160	94	58.8	300
比較例4-3	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	2.0	5	0.5	0.07	0.02	160	120	75.0	350
実施例4-5	$LiMn_{0.425}Ni_{0.425}Co_{0.1}B_{0.05}O_2$	1.0	9	1.0	0.18	0.14	157	118	75.2	700
実施例4-6	$LiMn_{0.425}Ni_{0.425}Co_{0.1}V_{0.05}O_2$	1.0	9	0.9	0.19	0.12	150	111	74.0	600
実施例4-7	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Al_{0.05}O_2$	1.0	9	1.0	0.19	0.13	155	113	72.9	700
実施例4-8	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Mg_{0.05}O_2$	1.0	9	1.0	0.19	0.13	152	114	75.0	700
実施例4-9	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Cr_{0.05}O_2$	1.0	9	1.0	0.19	0.14	152	114	75.0	650
実施例4-10	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Ti_{0.05}O_2$	1.0	9	1.0	0.19	0.15	154	112	72.7	650
実施例4-11	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Fe_{0.05}O_2$	0.9	9	0.9	0.19	0.11	150	109	72.7	650
実施例4-12	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Cu_{0.05}O_2$	0.9	9	1.0	0.20	0.10	151	115	76.2	620
実施例4-13	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Zn_{0.05}O_2$	0.9	9	1.0	0.19	0.12	153	120	78.4	650

また、(実施例１－１）の電池について、１．５Ａ（０．１Ｉｔ）で放電を行ったときの放電電圧変化を図６に、(実施例１－１０）の電池について、１．５Ａ（０．１Ｉｔ）で放電を行ったときの放電電圧変化を図７に、(実施例４－１）の電池について、１．５Ａ（０．１Ｉｔ）で放電を行ったときの放電電圧変化を図８に示す。

(第一実施形態について)

空間群Ｒ３／ｍ類似の層状構造を持つ正極活物質を用いた（実施例１－１）～（実施例１－１１）の電池と、空間群Ｃ２／ｍに属する層状構造を持つ正極活物質を用いた（比較例１－１）の電池とを比較すると、高率放電特性が大きく改善されていることがわかる。また、空間群Ｒ３／ｍ類似の層状構造を持つ正極活物質$LiMn_{0.5}Ni_{0.5}O_2$を用いた電池の中でも、(実施例１－１）～(実施例１－１１）及び（比較例１－３）～（比較例１－６）とを比較すると、比表面積の値を０．３m^2／ｇ以上とすることで、高率放電特性が顕著に改善されることがわかる。一方、前記比表面積の値が１．５m^2／ｇを越えると、充放電サイクル性能が急激に低下することがわかる。このことから、０．３m^2／ｇ以上１．５m^2／ｇ以下の比表面積を有する$LiMn_{0.5}Ni_{0.5}O_2$を正極活物質に用いると、良好なサイクル寿命と高い高率放電特性を兼ね備えた二次電池が提供できる。

また、同じく$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を用い、ＣｕＫα線を使用した粉末エックス線回折図の、$2\theta=18.6\pm1°$における回折ピークに対する$2\theta=44.1\pm1°$における回折ピークの相対強度比が異なる電池について電池性能を比べると、相対強度比が０．６以上となると、サイクル寿命が大きく向上することが分かる。また、前記相対強度比が１．１を越えると、高率放電特性値が低下する傾向となることがわかる。このことから、前記相対強度比を０．６以上１．１以下とすることにより、特に、良好なサイクル寿命と高い効率放電特性を兼ね備えた電池を提供できる。

また、$2\theta=18.6\pm1°$における回折ピークの半値幅が０．１３°以上であり、かつ、$2\theta=44.1\pm1°$における回折ピークの半値幅が０．１０°以上である場合、良好な高率放電特性が得られることがわかる。また、$2\theta=18$

．６±１°における回折ピークの半値幅が０．２０°より大きく、かつ、２θ＝４４．１±１°における回折ピークの半値幅が０．１７°より大きい場合、サイクル寿命が低下する傾向となることが分かる。このことから、２θ＝１８．６±１°における回折ピークの半値幅が０．１３～０．２０°であり、かつ、２θ＝４４．１±１°における回折ピークの半値幅が０．１０～０．１７°とすることにより、特に、良好なサイクル寿命と高い効率放電特性を兼ね備えた電池を提供できる。

なお、（比較例１－２）の電池は、高率放電特性が比較的良好なスピネルマンガンを正極の主たる活物質として用いている。この電池においては、スピネルマンガンから期待される通りの高率放電性能が得られていることから、本実施例及び比較例において、放電特性の律速が正極以外の構成要素である電解液や負極等によるものではないことが確認される。

（第二実施形態について）

$LiMn_{0.5}Ni_{0.5}O_2$を構成するＭｎ及びＮｉの一部を異種元素で置換した（実施例２－１）～（実施例２－７）の電池では、類似の物性を持つ正極活物質を用いた（実施例１－２）の電池と比べて、高率放電特性値が大きく向上することがわかる。この作用効果については必ずしも明らかではないが、Ｎｉ、Ｍｎと異なる少量の元素による置換は、リチウムイオン移動を向上させる働きがあるものと考えられる。

また、第二実施形態において、比表面積の値が０．３m^2／ｇを下回った（比較例２－１）の電池は、高率放電性能値が不十分であった。一方、比表面積の値が１．５m^2／ｇを越える（比較例２－２）の電池は、充放電サイクル性能が急激に低下することがわかる。

（第三実施形態について）

また、（実施例３－１）の電池は、（実施例１－１）～（実施例１－１１）の電池に比べて、高率放電特性が高く、ホウ素による元素置換の効果が認められる。

$LiMn_{0.5}Ni_{0.5}O_2$のＭｎ及びＮｉの一部を、ホウ素と、それ以外の元素とで

置換した（実施例３－２）～（実施例３－７）の電池では、さらに高率放電性能を改善できることがわかる。これは、Ｎｉ及びＭｎ以外の少量の異種元素による置換は、リチウムイオン移動を向上させる働きがあるものと考えられる。

また、第三実施形態において、比表面積の値が０．３m^2／ｇを下回った（比較例３－１）の電池は、高率放電性能値が不十分であった。一方、比表面積の値が１．５m^2／ｇを越える（比較例３－２）の電池は、充放電サイクル性能が急激に低下することがわかる。

なお、図１にみられるように、エックス線光電子分光法（ＸＰＳ）によるエッチング時間が約４００秒に達すると、ホウ素濃度が粒子内部と同程度にまで低減している。ここで、深さ方向のエッチング速度は０．０７ｎｍ（秒）である。このことから、本発明の効果を発現させるために必要な正極活物質粒子の表層部の厚さは、高々２８ｎｍ（＝０．０２８μｍ）あれば十分であることがわかる。正極活物質の平均粒径が９～１０μｍの場合、前記厚さは粒子の直径の約２％に相当する。

（第四実施形態について）

また、$LiMn_{0.5}Ni_{0.5}O_2$で表わされる複合酸化物にＣｏ成分を加えた$Li[Mn_xNi_yCo_z]O_2$で表わされる複合酸化物を正極活物質に用いた（実施例４－１）～（実施例４－４）の電池では、いずれも放電容量が、（実施例１－１）～（実施例１－１１）の電池に比べて大幅に増加した。また、結晶構造が安定になったためか、サイクル寿命も大きく向上した。

同じ組成式$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$で表わされ、比表面積の異なる複合酸化物を正極活物質に用いた（実施例４－１）、（実施例４－３）、（実施例４－４）、（比較例４－２）、（比較例４－３）について電池性能を比較すると、比表面積が１．５m^2／ｇを超えると、サイクル性能が急激に低下することがわかった。また、比表面積が０．３m^2／ｇを下回ると、高率放電性能が急激に悪くなることがわかった。このことから、複合酸化物の比表面積の値を０．３m^2／ｇ以上１．５m^2／ｇ以下とすることで、良好なサイクル性能と高い高率放電性能を兼ね備える非水電解質二次電池を提供できる。

Ｎｉ、Ｍｎ、Ｃｏ以外の異種元素Ｍ”を組成に加えた$LiMn_{0.425}Ni_{0.425}Co_{0.1}M''_{0.05}O_2$の組成式で表わされる複合酸化物を正極活物質に用いた（実施例４－５）～（実施例４－１０）の電池では、異種元素Ｍ”を添加していない（実施例４－１）の電池と比較して高率放電性能値がいずれも向上していることがわかる。この作用効果については必ずしも明らかではないが、Ｎｉ、Ｍｎと異なる少量の元素による置換は、リチウムイオン移動を向上させる働きがあるものと考えられる。

ところで、ホウ素を添加した実施例２－１，実施例３－１，実施例４－７の電池を解体し、電池を構成する各構成要素について元素分析を行った結果、負極表面付近からホウ素が検出された。このことから、合成時に添加したホウ素は、Ｍｎ及びＮｉと置換して構造を安定化させる効果よりも、むしろ、正極活物質粒子から溶出し、正極表面の状態を活性に変え、高率放電性能を向上させる効果を発現するものと考えられる。

なお、本発明の層状構造を有する活物質の場合、基本的にはＬｉは６ａサイトに、Ｍｎ、Ｎｉ、Ｃｏは６ｂサイトに、そしてＯは６ｃサイトを占有しているが、原理的には、Ｌｉが６ｂサイト中に拡散した形態もとりうる。その場合、Ｌｉは１価の価数であることから６ｂサイト中の不足する電荷は６ｃサイトの増減によって電荷中和される。

上記実施形態２の実施例においては、正極活物質における主構成物質に$Li[Mn_{0.475}Ni_{0.475}B_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.475}V_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.475}Al_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.475}Mg_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.475}Co_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.475}Cr_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.475}Ti_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.475}Li_{0.05}O_2]$ を用いることを記載したが、その他の異種元素Ｍを用いた場合についても同様な効果が得られる事が確認された。

上記実施形態３の実施例においては、正極活物質における主構成物質に$Li[Mn_{0.475}Ni_{0.475}B_{0.05}O_2]$、ホウ素の表面濃度が大きい$Li[Mn_{0.475}Ni_{0.475}B_{0.05}O_2]$、$Li[Mn_{0.475}Ni_{0.474}V_{0.05}B_{0.001}O_2]$、$Li[Mn_{0.475}Ni_{0.474}V_{0.05}Al_{0.001}O_2]$、$Li[Mn_{0.475}Ni_{0.474}V_{0.05}Mg_{0.001}O_2]$、$Li[Mn_{0.475}Ni_{0.474}V_{0.05}Co_{0.001}$

O_2]、Li[$Mn_{0.475}Ni_{0.474}Cr_{0.05}B_{0.001}O_2$]、Li[$Mn_{0.475}Ni_{0.474}Ti_{0.05}B_{0.001}O_2$]、を用いることを記載したが、その他の異種元素M'を用いた場合についても同様な効果が得られる事が確認された。

上記実施形態４の実施例においては、正極活物質における主構成物質にLi[$Mn_{0.45}Ni_{0.45}Co_{0.1}O_2$]、Li[$Mn_{0.425}Ni_{0.425}Co_{0.1}B_{0.05}O_2$]、Li[$Mn_{0.425}Ni_{0.425}Co_{0.1}V_{0.05}O_2$]、Li[$Mn_{0.425}Ni_{0.425}Co_{0.1}Al_{0.05}O_2$]、Li[$Mn_{0.425}Ni_{0.425}Co_{0.1}Mg_{0.05}O_2$]、Li[$Mn_{0.425}Ni_{0.425}Co_{0.1}Cr_{0.05}O_2$]、Li[$Mn_{0.425}Ni_{0.425}Co_{0.1}Ti_{0.05}O_2$]、Li[$Mn_{0.425}Ni_{0.425}Co_{0.1}Li_{0.05}O_2$]を用いることを記載したが、その他の元素を用いた場合についても同様な効果が得られる事が確認された。

ここでは、負極材料として人造黒鉛を用いた非水電解質二次電池について実施例を挙げたが、同様の効果は、その他の負極材料についても確認された。

なお、本発明は上記実施例に記載された活物質の出発原料、製造方法、正極、負極、電解質、セパレータ及び電池形状などに限定されるものではない。

＜産業上の利用可能性＞

本発明によれば、上記問題点を解決するためになされたものであって、高率充放電性能及び充放電サイクル性能に優れる高エネルギー密度の非水電解質二次電池を提供できる。

請 求 の 範 囲

1． Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物を主成分とする正極活物質であって、前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物のＢＥＴ法による比表面積が０．３m^2／ｇ以上１．５m^2／ｇ以下であることを特徴とする正極活物質。

2． 前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物であることを特徴とする請求の範囲第１項に記載の正極活物質。

3． 前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が異種元素で置換され、次の一般式；

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

（但し、Ｍは前記異種元素 ；

$x=0.001\sim0.1$ ； $x'=0.001\sim0.1$ ；

$y=0\sim0.1$ ； $y'=0\sim0.1$ ；

$x+x'+y+y'\leqq0.4$ ； $0\leqq z\leqq1$）

で示される組成の複合酸化物であることを特徴とする請求の範囲第１項に記載の正極活物質。

4． 前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が異種元素で置換され、次の一般式；

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

（但し、Ｍは前記異種元素 ；

$x=0.01\sim0.1$ ； $x'=0.01\sim0.1$ ；

$y=0\sim0.1$ ； $y'=0\sim0.1$ ；

$x+x'+y+y'\leqq0.2$ ； $0\leqq z\leqq1$）

で示される組成の複合酸化物であることを特徴とする請求の範囲第１項に記載の正極活物質。

5． 前記異種元素ＭがＢ，Ｍｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｏ，Ｃｕ及びＺｎから構成される群から選ばれる１種以上であることを特徴とする請求の範囲第３項または第４項に記載の正極活物質。

6． 前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される

複合酸化物を構成するＭｎ及びＮｉの一部が、異種元素並びにホウ素で置換され、次の一般式；

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

（但し、Ｍ’は前記異種元素　；

ｒ＝０．００１～０．１　；　ｒ´＝０．００１～０．１　；

ｓ＝０～０．１　；　ｓ´＝０～０．１　；

ｒ＋ｒ´＋ｓ＋ｓ´＋ｗ＋ｗ´≦０．４　；

ｗ＋ｗ´＝０．０００５～０．０１　；　０≦ｔ≦１）

で示される組成の複合酸化物であることを特徴とする請求の範囲第１項に記載の正極活物質。

７．　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$LiMn_{0.5}Ni_{0.5}O_2$で表される複合酸化物を構成するＭｎ及びＮｉの一部が、異種元素並びにホウ素で置換され、次の一般式；

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

（但し、Ｍ’は前記異種元素　；

ｒ＝０．０１～０．１　；　ｒ´＝０．０１～０．１　；

ｓ＝０～０．１　；　ｓ´＝０～０．１　；

ｒ＋ｒ´＋ｓ＋ｓ´＋ｗ＋ｗ´≦０．２　；

ｗ＋ｗ´＝０．０００５～０．０１　；　０≦ｔ≦１）

で示される組成の複合酸化物であることを特徴とする請求の範囲第１項に記載の正極活物質。

８．　前記異種元素Ｍ’がＭｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｏ，Ｃｕ及びＺｎから構成される群から選ばれる１種以上であることを特徴とする請求の範囲第６項または第７項に記載の正極活物質。

９．　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、$Li[Mn_cNi_dCo_eLi_aM''_b]O_2$（Ｍ”はＭｎ、Ｎｉ、Ｃｏ、Ｌｉ以外の元素、ｄ≦ｃ＋ｅ＋ａ＋ｂ、ｃ＋ｄ＋ｅ＋ａ＋ｂ＝１、０≦ａ≦０．０５、０≦ｂ≦０．０５、０．２≦ｃ≦０．５、０．０２≦ｅ≦０．４）で表される複合酸化物であることを特徴とする請求の範囲第１項に記載の正極活物質。

１０．　前記M”が、Ｂ，Ｍｇ，Ａｌ，Ｔｉ，Ｖ，Ｃｒ，Ｆｅ，Ｃｕ及びＺｎからなる群から選ばれる少なくとも１種の元素であることを特徴とする請求の範囲第９項に記載の正極活物質。

１１．　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物が、ＣｕＫα線を使用した粉末エックス線回折図の２θ＝１８．６±１°、３６．６±１°、３７．８±１°、３８．２±１°、４４．３±１°、４８．４±１°、５８．４±１°、６４．２±１°、６４．８±１°、６８．８±１°にピークを有する層状結晶構造であることを特徴とする請求の範囲第１項～第１０項のいずれかに記載の正極活物質。

１２．　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、ＣｕＫα線を使用した粉末エックス線回折図の、２θ＝１８．６±１°における回折ピークに対する２θ＝４４．１±１°における回折ピークの相対強度比が０．６以上１．１以下であることを特徴とする請求の範囲第１項～第１１項のいずれかに記載の正極活物質。

１３．　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物は、ＣｕＫα線を使用した粉末エックス線回折図の、２θ＝１８．６±１°における回折ピークの半値幅が０．１３°以上０．２０°以下であり、かつ、２θ＝４４．１±１°における回折ピークの半値幅が０．１０°以上０．１７°以下であることを特徴とする請求の範囲第１項～第１２項のいずれかに記載の正極活物質。

１４．　前記Ｌｉ－Ｍｎ－Ｎｉ系複合酸化物の粒径が３μｍ以上２０μｍ以下である請求の範囲第１項～第１３項のいずれかに記載の正極活物質。

１５．　請求の範囲第１項～第１４項のいずれかに記載の正極活物質を用いた非水電解質二次電池。

図 1

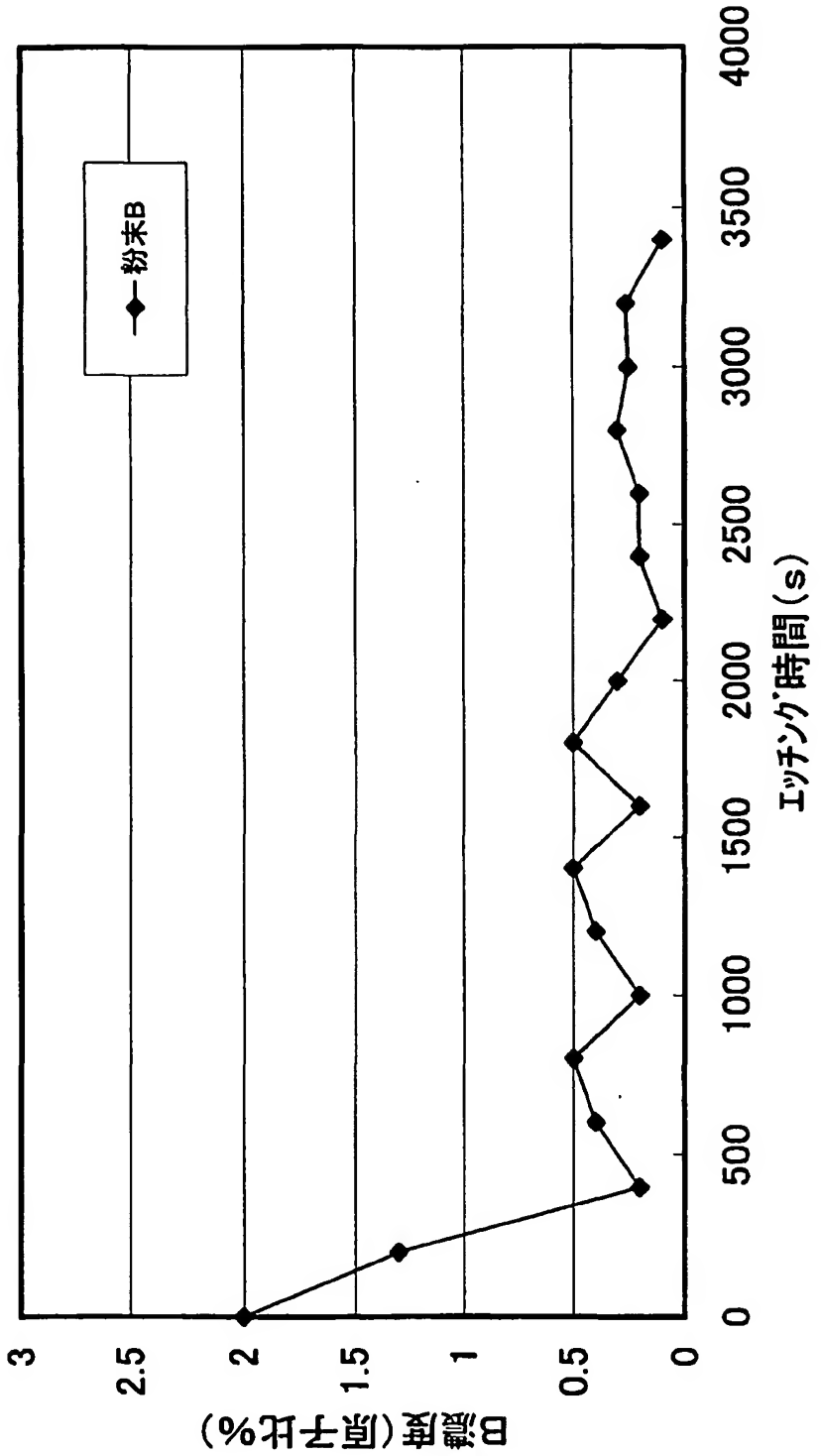

粉末B
B濃度(原子比%)
エッチング時間(s)
0
0.5
1
1.5
2
2.5
3
0
500
1000
1500
2000
2500
3000
3500
4000

図 2

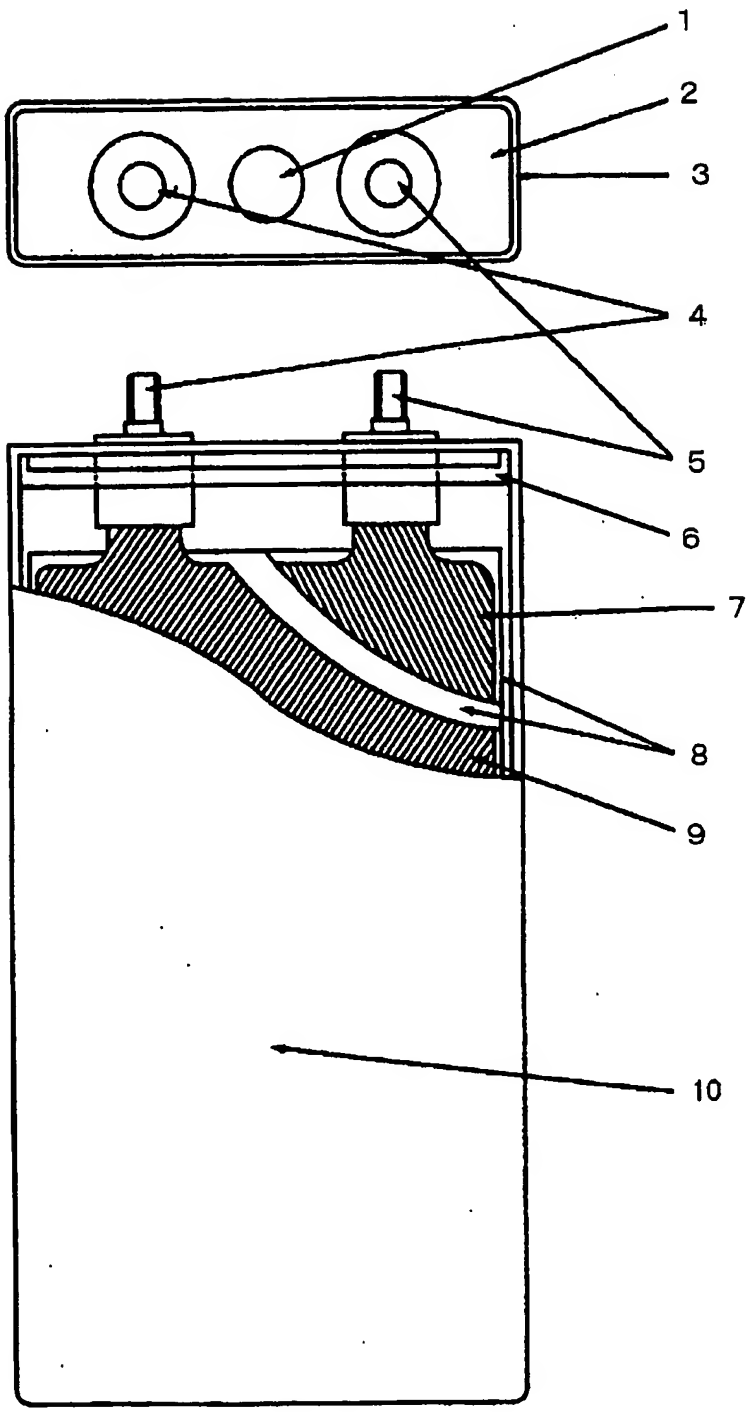


図 3

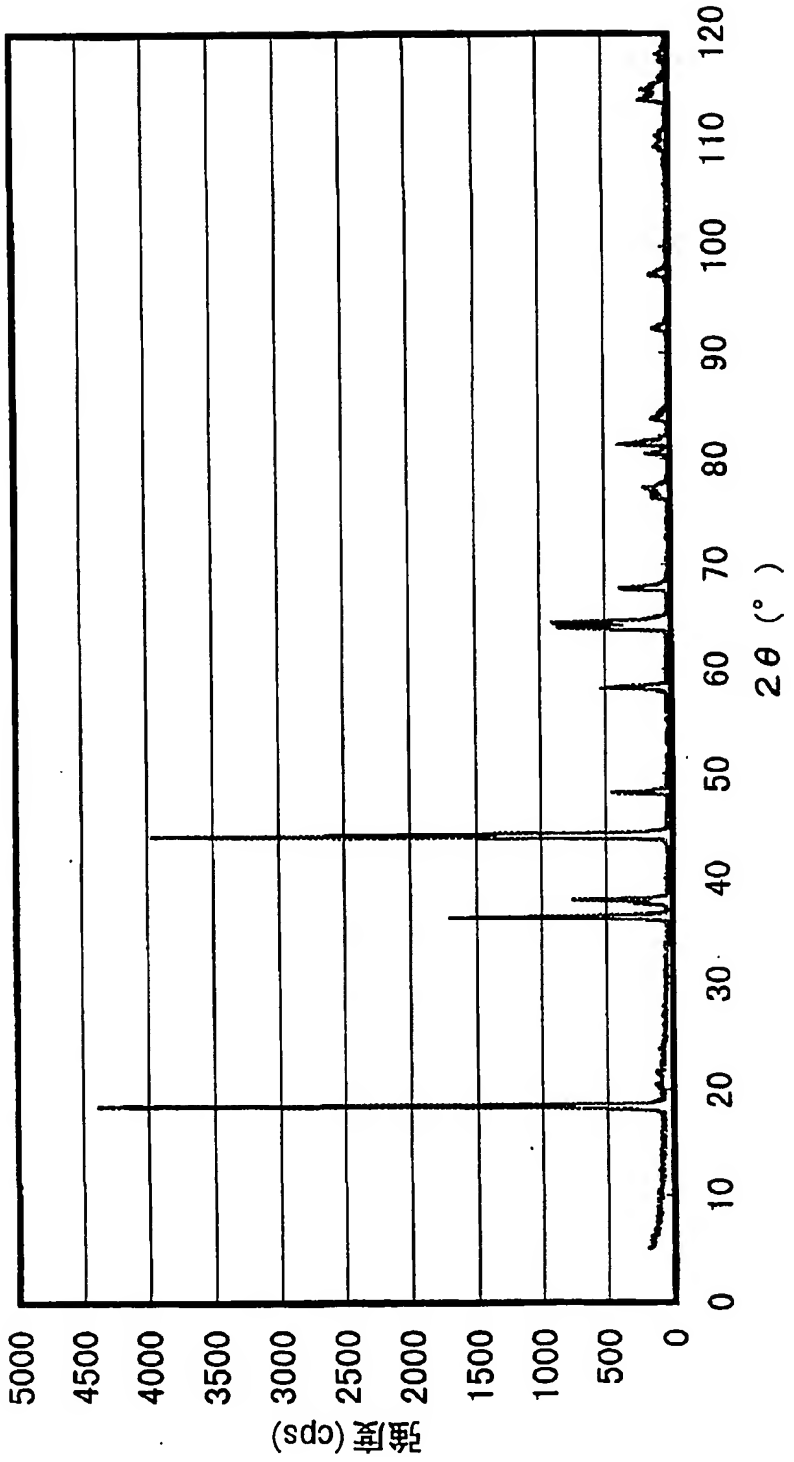

強度 (cps)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
100
110
120
2θ (°)

図 4

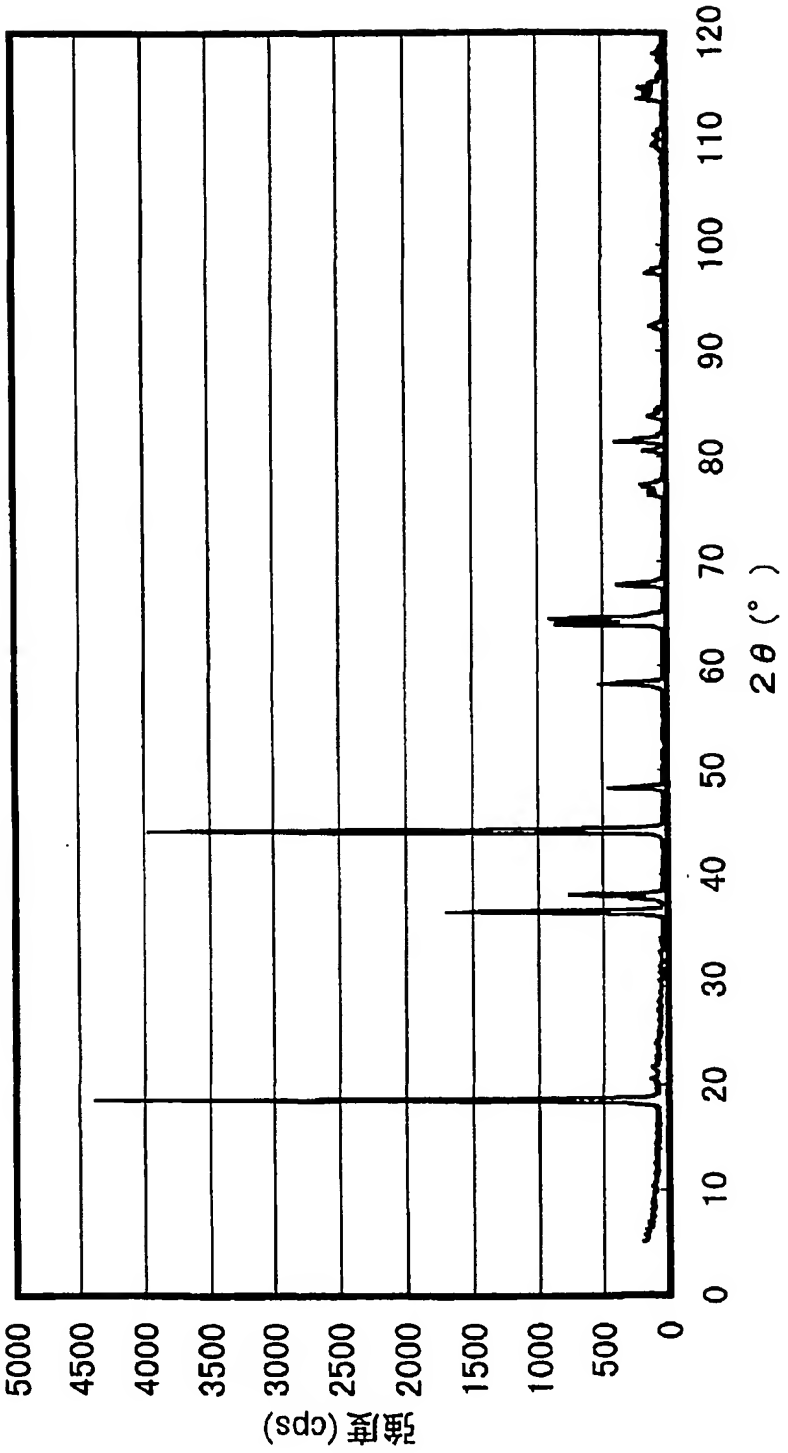

強度 (cps)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
100
110
120
2θ (°)

図 5

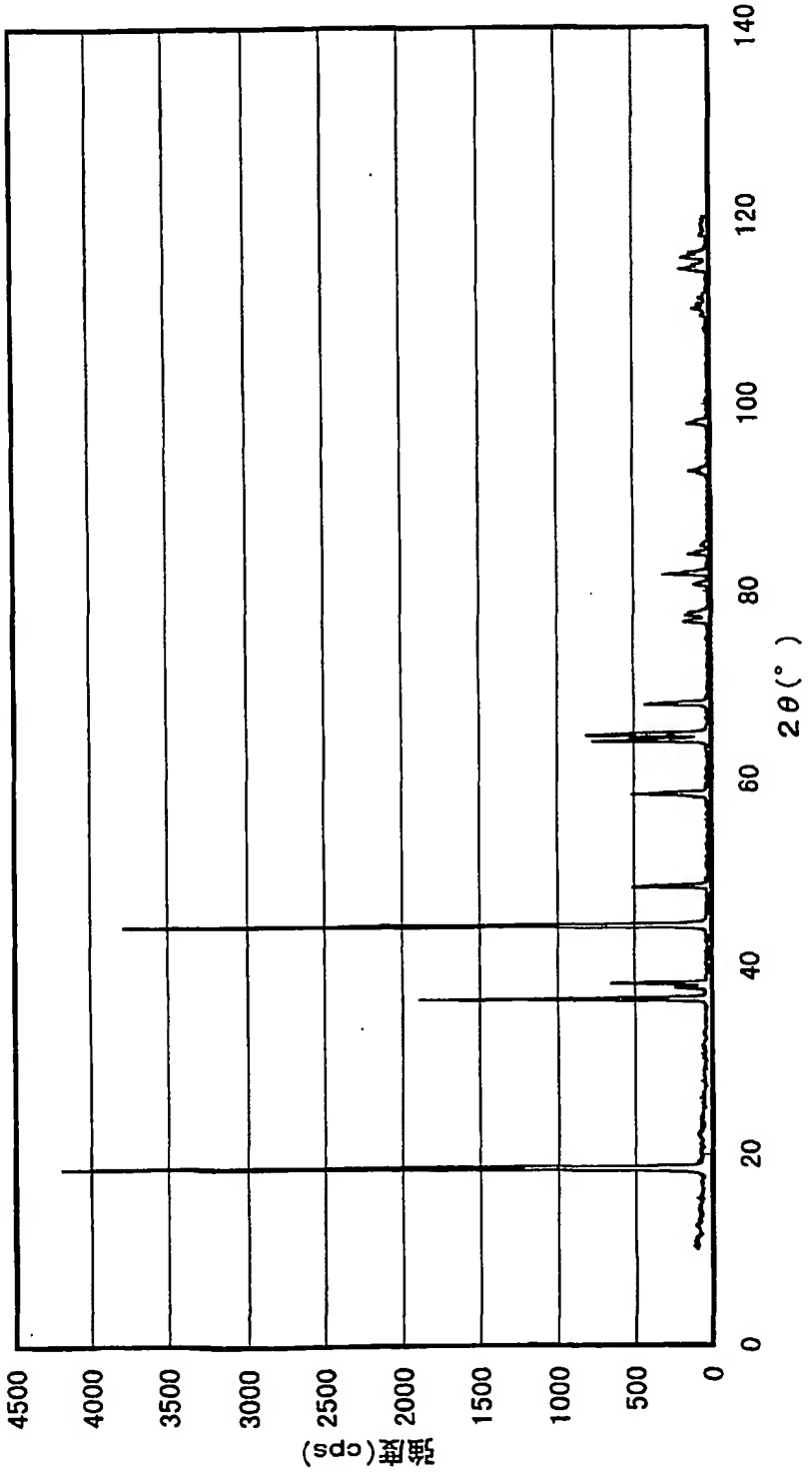

強度(cps)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
20
40
60
80
100
120
140
2θ(°)

図 6

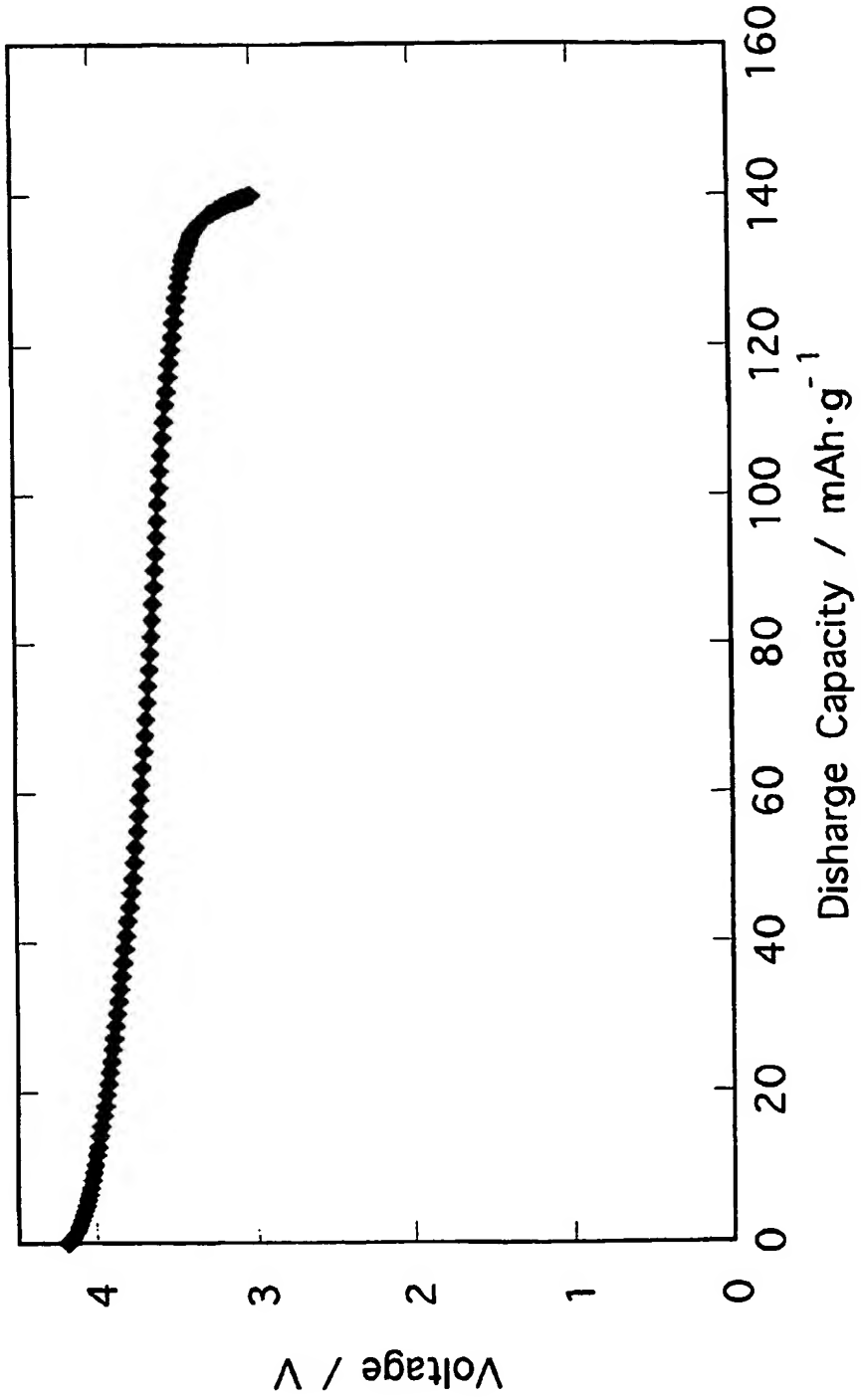

Voltage / V
0
1
2
3
4
Disharge Capacity / mAh·g-1
0
20
40
60
80
100
120
140
160

図 7

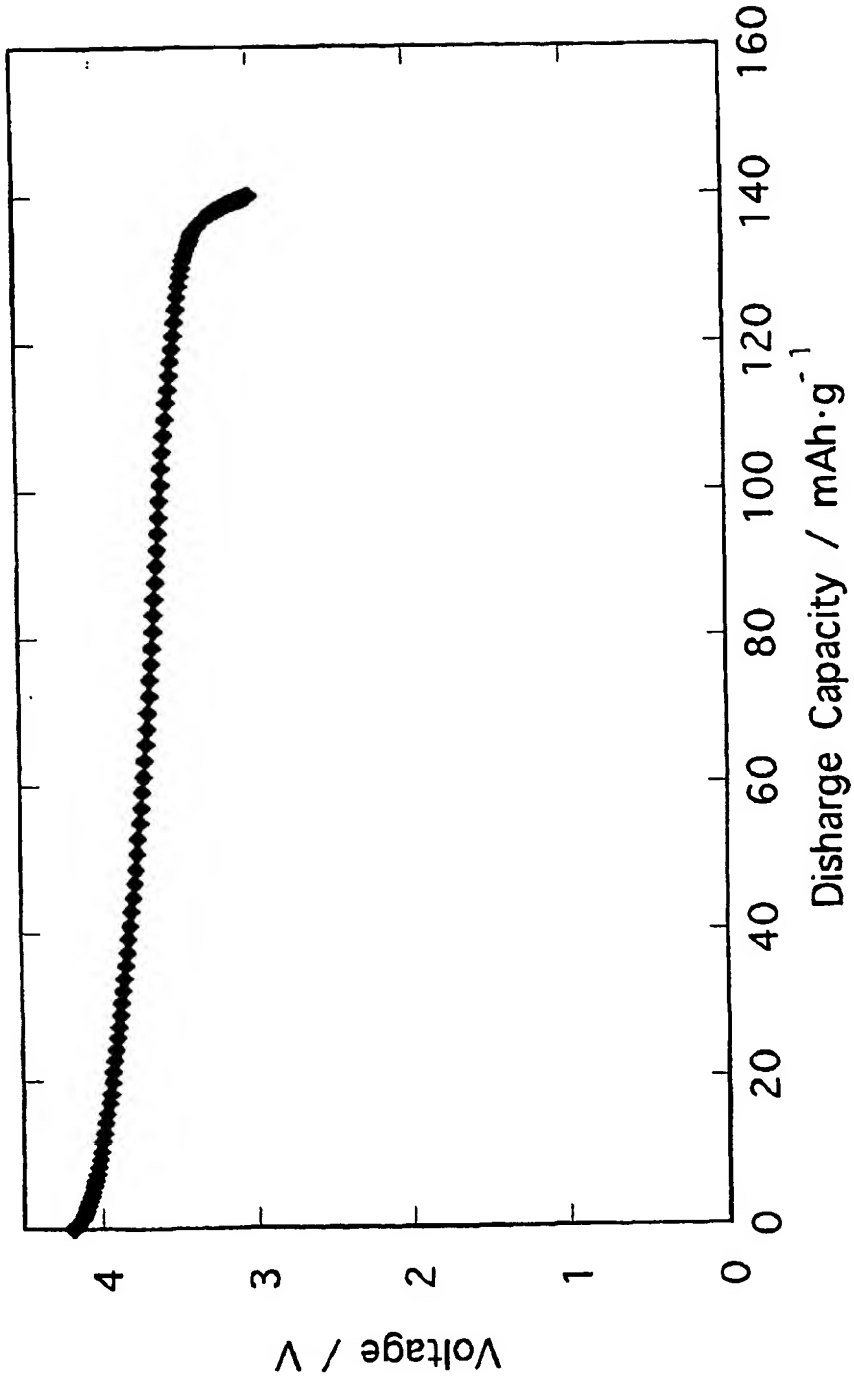
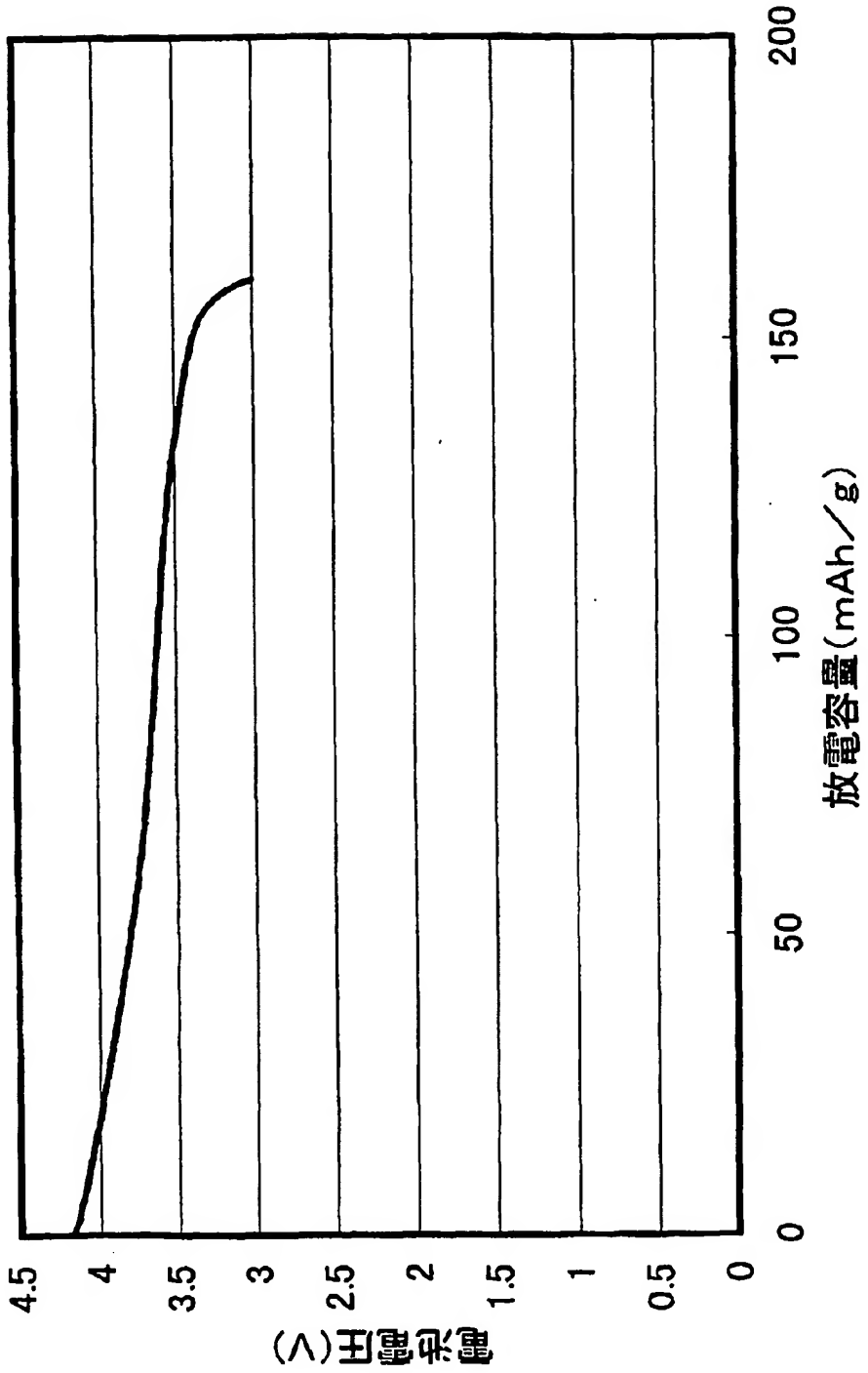

Voltage / V
0
1
2
3
4
Disharge Capacity / mAh·g-1
0
20
40
60
80
100
120
140
160

図 8



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP02/02284

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] H01M4/58, H01M4/02, H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] H01M4/58, H01M4/02, H01M10/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2002
Kokai Jitsuyo Shinan Koho	1971-2002	Jitsuyo Shinan Toroku Koho	1996-2002

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP 2000-195516 A (Sanyo Electric Co., Ltd.), 14 July, 2000 (14.07.00), Claims 1, 3; Par. Nos. [0020], [0026] (Family: none)	1-5,14,15 2-12,14,15 13
Y	JP 05-242891 A (Sanyo Electric Co., Ltd.), 21 September, 1993 (21.09.93), Par. No. [0016]; Fig. 3 (Family: none)	9,10
Y A	JP 09-199127 A (Matsushita Electric Industrial Co., Ltd.), 31 July, 1997 (31.07.97), Claim 1 (Family: none)	2-8,11,12,14,15 13

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 May, 2002 (21.05.02)	04 June, 2002 (04.06.02)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP02/02284

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	JP 2002-42813 A (Matsushita Electric Industrial Co., Ltd.),	2-5,11,12, 14,15
P,A	08 February, 2002 (08.02.02), Claims 1, 3; Par. No. [0014] (Family: none)	13
A	EP 554906 A1 (Matsushita Electric Industrial Co., Ltd.), 11 August, 1993 (11.08.93), Claim 1 & US 5393622 A & JP 06-96768 A Claim 1	1-15

国際調査報告

国際出願番号 PCT／JP02／02284

A. 発明の属する分野の分類（国際特許分類（IPC））

Int. Cl' H01M 4／58,H01M 4／02,H01M 10／40

B. 調査を行った分野

調査を行った最小限資料（国際特許分類（IPC））

Int. Cl' H01M 4／58,H01M 4／02,H01M 10／40

最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報 1926－1996年
日本国公開実用新案公報 1971－2002年
日本国登録実用新案公報 1994－2002年
日本国実用新案登録公報 1996－2002年

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

C. 関連すると認められる文献

引用文献のカテゴリー＊	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求の範囲の番号
X Y A	JP 2000-195516 A（三洋電機株式会社），2000．07．14，請求項1，3，【0020】，【0026】，（ファミリーなし）	1～5, 14, 15 2～12, 14, 15 13
Y	JP 05-242891 A（三洋電機株式会社），1993．09．21，【0016】，図3，（ファミリーなし）	9, 10
Y A	JP 09-199127 A（松下電器産業株式会社），1997．07．31，請求項1，（ファミリーなし）	2～8, 11, 12, 14, 15 13

[x] C欄の続きにも文献が列挙されている。 [ ] パテントファミリーに関する別紙を参照。

＊ 引用文献のカテゴリー
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「L」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す）
「O」口頭による開示、使用、展示等に言及する文献
「P」国際出願日前で、かつ優先権の主張の基礎となる出願の日の後に公表された文献
「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの
「X」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの
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「&」同一パテントファミリー文献

国際調査を完了した日	国際調査報告の発送日
21．05．02	04.06.02

国際調査機関の名称及びあて先	特許庁審査官（権限のある職員）	4X	3132
日本国特許庁（ISA／JP） 郵便番号100－8915 東京都千代田区霞が関三丁目4番3号	天野 斉 印		
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様式PCT／ISA／210（第2ページ）（1998年7月）

国際調査報告

国際出願番号　ＰＣＴ／ＪＰ０２／０２２８４

Ｃ（続き）．　関連すると認められる文献

引用文献のカテゴリー＊	引用文献名　及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求の範囲の番号
P,Y	JP 2002-42813 A（松下電器産業株式会社），２００２．０２．０８ 請求項１，３，【００１４】，（ファミリーなし）	2～5,11,12,14,15
P,A		13
A	EP 554906 A1(MATSUSHITA ELECTRIC INDUSTRIAL CO.,LTD.), １９９３．０８．１１,請求項１，＆ US 5393622 A ＆ JP 06-96768 A ,請求項１	1～15

様式ＰＣＴ／ＩＳＡ／２１０（第２ページの続き）（１９９８年７月）

INTERNATIONAL PUBLICATION WO02/073718 A1

POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY CELL COMPRISING THE SAME

[Translated from Japanese]

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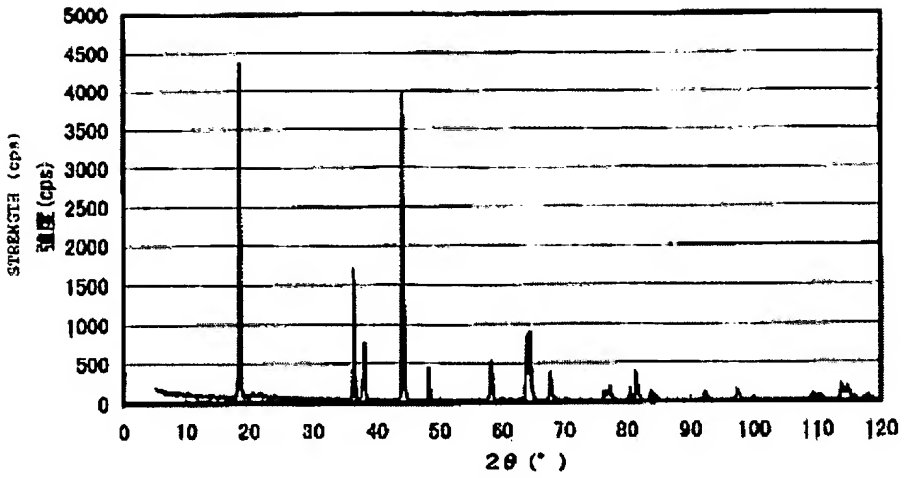
84) Appointed Countries (Wide regions): ARIPO patents (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasia patents (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European Patents (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patents (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, ML, MR, NE, SN, TD, TG).

Attachment International Search Report

For two letter codes and other abbreviation, see "Guide Notes for Codes and Abbreviations" listed on front of each PCT Gazette bulletin.

(54) Title: POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY CELL COMPRISING THE SAME [Seikyoku kasseibutsu oyobi koreo mochiita hisuiden'kaishitsu nijiden'chi]

(57) Abstract: [English, included] A positive electrode active material for producing a nonaqueous electrolyte secondary cell exhibiting an excellent high-rate charging/discharging performance and an excellent charging/discharging cycle performance and having a high energy density, and a nonaqueous electrolyte secondary cell
exhibiting an excellent high-rate charging/discharging performance and an excellent charging/discharging cycle performance and having a high energy density. The main component of the positive electrode active material is a Li-Mn-Ni composite oxide, and the positive electrode active material is characterized in that the specific surface of the Li-Mn-Ni composite oxide measured by the BET method is 0.3 m^2/g or above and 1.5 m^2/g or below. The nonaqueous electrolyte secondary cell comprises such a positive electrode active material.



[Translator's note: vertical axis should be labeled "Intensity (cps)"]

(57) Abstract:

Production of a positive electrode active material capable of producing a nonaqueous secondary cell with high energy density exhibiting an excellent high-rate charging/discharging performance and a nonaqueous secondary cell with high energy density exhibiting an excellent high-rate charging/discharging performance and an excellent charging/discharging cycle performance.

A positive electrode active material mainly comprising a Li-Mn-Ni type composite oxide, and the positive electrode active material is characterized by the fact that the specific surface of the Li-Mn-Ni composite oxide measured by the BET method is 0.3 m^2/g or above and 1.5 m^2/g or below, and nonaqueous electrolyte secondary cell comprising the same.

[p. 1]

Specification

Positive electrode active material and nonaqueous secondary cell comprising the same

<Technical Field>

The present invention pertains to a positive electrode active material and a nonaqueous secondary cell comprising the same.

<Background>

Nonaqueous secondary cells such as lithium secondary cells exhibit high energy density and high voltage and are widely used as the power sources for compact portable terminals, mobile communication devices, etc. For the positive electrode active material of the lithium secondary cell, a stable crystalline structure and high electrochemical working performance are required despite repeated insertion and removal of lithium. For those with an operating voltage of around 4 V, transition metal oxides with a basic structure of a layer comprising lithium cobalt oxide, lithium nickel oxide, or lithium manganese oxide having spinel structure are known.

Currently, as positive electrode active materials for nonaqueous secondary cells with an operating voltage of around 4 V, composite oxides of lithium and a transition metal such as $LiCoO_2$, $LiNiO_2$, $LiMnO_2$ and $LiMn_2O_4$ are known. In particular, among positive electrode active materials with α-$NaFeO_2$ structure from which a high energy density can be expected, lithium cobalt composite oxide indicated by $LiCoO_2$ is widely used for consumer lithium ion cells, but cobalt is a rare metal and the cost is high. Furthermore, lithium nickel composite oxide indicated by $LiNiO_2$, etc. lack stability at high temperatures, thus, safety is hard to come by and practical application is not possible. And furthermore, lithium manganese oxide having a spinel structure indicated by $LiMn_2O_4$, etc. is an inexpensive and safe positive electrode active material, but the energy density per unit weight is approximately 70% that of lithium cobalt composite oxide, and is used in some areas, but is not widely applied.

On the other hand, principally, high capacity can be expected from $LiMnO_2$, and the safety level is high; thus, it is widely studied. For the aforementioned $LiMnO_2$, β-$NaMnO_2$ type rhombic system layer structure having a zigzag layer structure, and α-$NaFeO_2$ type monoclinic system structure having halite layer structure are known.

[p. 2]

A higher capacity can be expected from the aforementioned $LiMnO_2$ having rhombic system structure than that of the aforementioned $LiMn_2O_4$, but when charge/discharge is

repeated, slow conversion to the spinel phase occurs; thus, stability with regard to the charge/discharge cycle becomes inferior. Furthermore, a poor high efficiency charge/discharge performance in $LiMnO_2$ having the aforementioned monoclinic system structure, and reduction in capacity that accompanies the charge/discharge cycle are reported in, for example, Chiang, Y-M.; Sadoway, D.R.; Jang, Y-I.; Huang, B.; Wang, H. High Capacity, Temperature-Stable Lithium Aluminium [sic] Manganese Oxide Cathodes for Rechargeable Batteries. Electrochem. Solid-State Lett. 2(3), 1999, 107-110.

In order to eliminate the above-mentioned problems, a technology in which the Mn in $LiMnO_2$ is replaced with Al, Fe, Co, Ni, Mg, or Cr in an amount in the range of $1-y(0.5 \leq y \leq 1)$, and at the same time, a voltage of 4.0 V to 4.8 V is applied between the positive electrode and the negative electrode at a temperature of 60 to 100°C and the change in crystalline structure is accelerated and improvement in high efficiency charge/discharge performance is achieved is disclosed in Japanese Kokai [Unexamined] Patent Application No. 2001-23617. However, high efficiency charge/discharge performance remains insufficient despite the above-mentioned technologies.

Furthermore, the aforementioned lithium manganese oxide has many technical problems associated with it upon application as well. Poor cycle performance and storage performance, especially at high temperatures, pose problems.

Furthermore, when $LiNi_{1-\alpha}Mn_{\alpha}O_2$ having the crystal structure of the space group R3/m is considered as a structure where a part of the Ni in $LiNiO_2$ is replaced with Mn, baking at a temperature of 800°C or above is required to secure the replacement of the Ni site with Mn. However, Ni or Mn enters the site in the crystal where Li is normally located when the above-mentioned high temperature is used, and the crystalline structure is disturbed, and capacity or cycle performance is reduced. A technology in which 0.05 to 0.30 is used for the value of the aforementioned α and baking is done at a temperature in the range of 600°C to 800°C is disclosed in Japanese Kokai [Unexamined] Patent Application No. Hei 8-171910, but the cycle

performance remains inadequate despite the aforementioned technology.

As a means to eliminate the above-mentioned problems, technology concerning the electrochemical performance of $LiMn_aNi_bCo_cO_2$ where a part of Ni in $LiNiO_2$ is replaced with Mn and Co is known. For example, a report on Li composite oxide concerning a, b, c are such that $0.02 \leq a \leq 0.5$, $0.02 \leq b/(b+c) \leq 0.9$, $b > 0.34$ and $a+b+c=1$ is disclosed in Japanese Patent Application No. 3244314. However, according to the follow-up study by the present inventors, thermal stability at the time of charging remains inadequate. The reason for this is not well understood, but it is hypothesized that the method of manufacturing the Li composite oxide in the aforementioned report includes mechanical mixing of solid materials, and diffusion of the metal element is incomplete at the time of the baking process that follows and partial phase separation occurs, and as a result, thermal stability becomes inferior. Furthermore, the particles of the Li composite produced by excessive pulverization of the raw material become very fine, and when the said material is used as the positive electrode of cell, a side reaction such as oxidation decomposition of electrolyte occurs since the positive electrode comes in full contact with the electrolyte, and deterioration with time is likely to occur as well.

Furthermore, among $LiMn_aNi_bCo_cO_2$ compositions, a report concerning $LiCo_{0.33}Ni_{0.33}Mn_{0.33}O_2$ composition is Yoshinari Makimura, Naoaki Yabuuchi, Tsutomu Ohzuku, Yukinori Kayama, Isao Tanak, and Hirohiko Adachi, Lithium Insertion Material of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$
for Advanced Batteries; (II) Synthesis and Characterization as a Possible Alternative to $LiCoO_2$, The 42th [sic] Battery Synposium [sic] in Japan, 2118, 2119(2001). The above-mentioned Li composite oxide is produced by mixing a coprecipitate compound produced by adding an alkali to an aqueous solution of Mn, Ni, and Co with a Li compound and providing a heat treatment.

However, definition of the properties on the Li composite oxide produced is not included in the aforementioned report. The lattice volume of the above-mentioned Li composite oxide is reduced by charging and increased by discharging; thus, the trapping speed of the Li in the active

material at the time of discharging is significantly reduced in comparison to the removal speed of Li at the time of charging. Therefore, when the maximum caution is taken for the factors responsible to have a high influence on the trapping speed of Li to the positive electrode as in the contact interfacial state of the active material and electrolyte, it is not possible to produce a cell having an adequate charge/discharge performance. Thus, it is essential to define the properties of the active material that determines the above-mentioned factors upon application of the cell in which the above-mentioned active material is used as the positive electrode.

[p. 4]

It should be noted that "R3/m" is used in the present specification where the horizontal bar is to be applied above the 3 of "R3m" to indicate space group for convenience.

The present invention is to eliminate the above-mentioned existing problems, and the purpose of the present invention is to produce a positive electrode active material for producing a nonaqueous electrolyte secondary cell exhibiting excellent high-rate charging/discharging performance and an excellent charging/discharging cycle performance and having a high energy density, and a nonaqueous electrolyte secondary cell
exhibiting an excellent high-rate charging/discharging performance and an excellent charging/discharging cycle performance and having a high energy density.

<Disclosure of the invention>

As a result of much research conducted by the present inventors in an effort to eliminate the above-mentioned existing problems, they discovered that a nonaqueous secondary cell having excellent cell performance could be produced when properties of a positive electrode active material having a specific structure were specified, and as a result, the present invention was accomplished. In other words, the technical structure and effect of the present invention are as described below provided that the assumption is included that the present invention is not limited to the correctness/incorrectness of the working mechanism.

(1) A positive electrode active material mainly comprising a Li-Mn-Ni type composite

oxide, and the positive electrode active material is characterized by the fact that the specific surface of the Li-Mn-Ni composite oxide measured by the BET method is 0.3 m^2/g or above and 1.5 m^2/g or below.

(2) The positive electrode active material described in (1) above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide is the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$.

(3) The positive electrode active material described in (1) above characterized by the fact that a part of Mn and Ni that comprise the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and is a composite oxide with a composition indicated by the following general formula.

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

(Wherein, M is the aforementioned dissimilar element;

$x=0.001$ to 0.1 ; $x'=0.001$ to 0.1 ;

$y=0$ to 0.1 ; $y'=0$ to 0.1 ;

$x+x'+y+y' \leq 0.4$; $0 \leq z \leq 1$)

[p. 5]

(4) The positive electrode active material described in the (1) above characterized by the fact that a part of Mn and Ni that comprises the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and is a composite oxide with a composition indicated by the following general formula.

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

(Wherein, M is the aforementioned dissimilar element;

$x=0.01$ to 0.1 ; $x'=0.01$ to 0.1 ;

$y=0$ to 0.1 ; $y'=0$ to 0.1 ;

$x+x'+y+y' \leq 0.2$; $0 \leq z \leq 1$)

(5) The positive electrode active material described in the aforementioned (3) or (4)

characterized by the fact that the aforementioned dissimilar element M is one or more elements selected from the group consisting of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, and Zn.

(6) The positive electrode active material described in the above-mentioned (1) characterized by the fact that a part of Mn and Ni that comprise the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and boron and is a composite oxide with a composition indicated by the following general formula.

$$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$$

(Wherein, M' is the aforementioned dissimilar element;

$r=0.001$ to 0.1 ; $r'=0.001$ to 0.1 ;

$s=0$ to 0.1 ; $s'=0$ to 0.1 ;

$r+r'+s+s'+w+w' \leq 0.4$;

$w+w'=0.0005$ to 0.01 ; $0 \leq t \leq 1$)

(7) The positive electrode active material described in the (1) above characterized by the fact that a part of Mn and Ni that structures the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and boron and is a composite oxide with the composition indicated by the following general formula.

$$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$$

[p. 6]

(Wherein, M' is the aforementioned dissimilar element;

$r=0.01$ to 0.1 ; $r'=0.01$ to 0.1 ;

$s=0$ to 0.1 ; $s'=0$ to 0.1 ;

$r+r'+s+s'+w+w' \leq 0.2$;

$w+w'=0.0005$ to 0.01 ; $0 \leq t \leq 1$)

(8) The positive electrode active material described in the above-mentioned (6) or (7)

characterized by the fact that the aforementioned dissimilar element M' is one or more elements selected from the group consisting of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, and Zn.

(9) The positive electrode active material described in the (1) above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide is a composite oxide indicated by $Li[Mn_cNi_dCo_eLi_aM''_b]O_2$ (Wherein, M'' is an element other than Mn, Ni, Co or Li, $d \leq c+e+a+b$, $c+d+e+a+b=1$, $0 \leq a \leq 0.05$, $0 \leq b \leq 0.05$, $0.2 \leq c \leq 0.05$, $0.02 \leq e \leq 0.4$).

(10) The positive electrode active material described in the above-mentioned (9) characterized by the fact that the aforementioned M'' is one or more elements selected among the group consisting of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, and Zn.

(11) The positive electrode active material described in one of (1) to (10) above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide has a layer crystalline structure having peaks at $2\theta = 18.61\pm1°$, $36.6\pm1°$, $37.8\pm1°$, $38.2\pm1°$, $44.3\pm1°$, $48.4\pm1°$, $58.4\pm1°$, $64.2\pm1°$, $64.8\pm1°$, $68.8\pm1°$ on the X-ray diffraction chart that utilizes CuKα ray.

(12) The positive electrode active material described in one of (1) to (11) above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide has a relative intensity ratio of the diffraction peak of $2\theta=44.1\pm1°$ for the diffraction peak of $2\theta=18.6\pm°$ on the powder X-ray diffraction chart that utilizes CuKα rays.

(13) The positive electrode active material described in one of (1) to (12) above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide has the half-bandwidth of the diffraction peak at $2\theta=18.6\pm1°$ in the range of 0.13° to 0.20° and the half band width of the diffraction peak at $2\theta=44.1\pm1°$ in the range of 0.10° to 0.17° on the powder X-ray diffraction chart that utilizes CuKα rays.

[p. 7]

(14) The positive electrode active material described in one of (1) to (13) above characterized by the fact that the particle diameter of the aforementioned Li-Mn-Ni type

composite oxide is in the range of 3 μm to 20 μm.

(15) The nonaqueous secondary cell that utilizes the positive electrode active material described in one of (1) to (14) above.

The present inventors placed their focus on the $LiMnO_2$ from which high capacity can be expected, and as an element used to substitute Mn, Ni having good solubility with Mn and operating potential of around 4 V was selected. As a result, it was confirmed that the operating potential was 4.3 V to 3.0 V and good compatibility with conventional lithium ion cells was achieved in $LiMn_{0.5}Ni_{0.5}O_2$ where the ratio of the substitution was 50% and a high-rate discharge capacity of 140 mAh/g could be achieved. However, charge/discharge cycle performance was inadequate. It was hypothesized that elution of Mn occurred from the positive electrode active material as a result of repeated charge/discharge and that an increase in electrode interfacial resistance was initiated.

Based on the above background, and as a result of much research done by the present inventors, in an effort to eliminate the above-mentioned existing problems, on the relationship between $LiMn_{0.5}Ni_{0.5}O_2$ having different properties and compositions where a part of Ni and Mn elements that comprise $LiMn_{0.5}Ni_{0.5}O_2$ replaced with other elements (hereinafter referred to as Li-Mn-Ni type composite oxide, at times) and the charge/discharge cycle performance, and to their surprise, they discovered that a very stable charge/discharge cycle performance could be achieved when the value of the specific surface area was specified. In other words, excellent charge/discharge cycle performance can be achieved when the value of the aforementioned specific surface area is specified at 1.5 m^2/g or below.

The above-mentioned effect achieved cannot be fully explained, but it is hypothesized that the area of the positive electrode active material Li-Mn-Ni type composite oxide that comes in contact with the electrolyte is reduced as a result of reduction in the specific surface area, and oxidation decomposition of the electrolyte is controlled, and furthermore, the moisture slightly adsorbed to the surface of the grain of the aforementioned positive electrode active material is

reduced with a reduction in the specific surface area; thus, formation ratio of the hydrofluoric acid (HF) in the cell due to moisture is reduced, and decomposition reaction of Mn due to the above-mentioned acid is less likely to occur.

[p. 8]

It was further recognized that high discharge capacity could be retained even when high-rate discharge of 2 It (0.5 hr) was carried out when the value of the aforementioned specific surface area was defined at 0.3 m^2/g or above.

Furthermore, when further research was conducted by the present inventors on the composition where a part of Ni and Mn among elements that comprise the $LiMn_{0.5}Ni_{0.5}O_2$ among Li-Mn-Ni type composite oxide was replaced with other dissimilar elements, to their surprise, a further improvement in the high-rate discharge performance was possible when the type of the aforementioned dissimilar elements was specified.

The above-mentioned effect cannot be fully explained, but the atomic radius, that is, the size of the aforementioned dissimilar element is different from the atomic radius of Mn or Ni; thus, it has an effect on the layer structure of the positive electrode active material, the mobility path of the Li ion is affected, and ion conduction is improved. Furthermore, the atomic radius, that is, the size of the aforementioned dissimilar elements other than Mn and Ni vary; thus, it seems that distortion based on expansion or contraction of the active crystal that accompanies the charge/discharge process is modified as a result of the inclusion of elements with different size.

It is further hypothesized that the close relationship of surface composition is based on the fact that the exchange of the Li ion is achieved at the boundary between the positive electrode active material particle and the electrolyte.

Furthermore, when a further study of the baking conditions, type, and composition of dissimilar metal elements other than Li, Mn, and Ni added at the time of synthesis of $LiMn_{0.5}Ni_{0.5}O_2$ was carried out, it was discovered that the structure of the crystal produced varied widely and a further increase in the charge/discharge cycle performance was made possible

depending on the type of crystal. In specific terms, it was confirmed that an excellent cycle performance could be achieved when the Li-Mn-Ni type composite oxide has a layer crystal structure having peaks at $2\theta = 18.6\pm1°$, $36.6\pm1°$, $37.8\pm1°$, $38.2\pm1°$, $44.3\pm1°$, $48.4\pm1°$, $58.4\pm1°$, $64.2\pm1°$, $64.8\pm1°$, $68.8\pm1°$ on the powder X-ray diffraction chart that utilizes CuKα ray.

[p. 9]

The above-mentioned effect achieved cannot be fully explained, but it seems that distortion is insignificant and the crystal structure itself is stable in crystals having the aforementioned powder X-ray diffraction pattern. Furthermore, it seems that the structure can be further stabilized, and extraction of lithium from the aforementioned crystalline structure can be promoted at a lower potential and as a result, an increase in the charge/discharge capacity is achieved when Co is added.

Furthermore, the crystalline structure varies widely even when the same component is used when the baking temperature is from 850°C to 1000°C, and the shape of the change in potential at the time of charge/discharge varies widely as well. In particular, the high-rate discharge performance is influenced by a slight change in the temperature and baking time at the time of the aforementioned baking.

Based on the above-mentioned background, the present inventors believe that the crystalline structure is influenced by the baking conditions, and placed their focus on the relative intensity ratio of the diffraction peak of $2\theta=44.1\pm1°$ for the diffraction peak of $2\theta=18.6\pm1°$ on the powder X-ray diffraction chart that utilizes CuKα rays for the powder produced after baking, and to their surprise, they discovered that an obvious increase in the high-rate discharge performance was observed when a lithium- manganese-nickel composite oxide having the aforementioned relative intensity of 1.1 or below was used.

The above-mentioned effect cannot be fully explained, but it seems that shifting of the lithium ion inside the solid material is facilitated when the aforementioned relative intensity is 1.1 or below.

However, when the aforementioned relative intensity is 0.6 or below, shifting of the lithium ion inside the solid material is inhibited due to slow crystal growth and charge/discharge cycle performance is reduced. Therefore, when a positive electrode active material having the aforementioned relative intensity in the range of 0.6 to 1.1 is used, production of a nonaqueous secondary cell having excellent high-rate discharge performance and excellent charge/discharge cycle performance is made possible.

Furthermore, it seems that the half bandwidth at $2\theta=18.6\pm1°$ and $2\theta=44.1\pm1°$ reflects the growth and crystal diameter of the positive electrode active material used for the cell of the present invention, and that the higher the half bandwidth, the lower the crystal diameter; but, to their surprise, it was confirmed that exceptionally good high-rate discharge performance and charge/discharge cycle performance was achieved when the half bandwidth of the diffraction peak at $2\theta=18.6\pm1°$ is in the range of 0.13° to 0.20° and the half bandwidth of the diffraction peak at $2\theta=44.1\pm1°$ is in a 0.10° to 0.17°.

[p. 10]

The above-mentioned effect cannot be fully explained, but it seems that shifting of the Li ion inside the solid material is facilitated when the half bandwidth of the diffraction peak at $2\theta=18.6\pm1°$ is 0.20° or below and at the same time, the half band width of the diffraction peak at $2\theta=44.1\pm1°$ is 0.17° or below, and improvement in high-rate discharge performance is made possible, but charge/discharge cycle performance is reduced due to the reduced stability of the crystal. Thus, an appropriate shifting of Li ion in the crystal and an adequate crystal stability can be achieved and excellent high-rate discharge performance and charge/discharge cycle performance can be achieved when the half bandwidth of the diffraction peak at $2\theta=18.6\pm1°$ is 0.13° or above and at the same time, the half band width of the diffraction peak at $2\theta=44.1\pm1°$ is 0.10° or above.

<Brief description of figures>

Fig. 1 shows the analysis results for the positive electrode active material used in the

present invention based on the X-ray photoelectric spectral (XPS). Fig. 2 is a partial cross-section view of the cells of the working examples and comparative examples. Fig. 3 is an X-ray analysis chart of the positive electrode active material of Working Example 1-1. Fig. 4 is the X-ray analysis chart of the positive electrode active material of Working Example 1-10. Fig. 5 is the X-ray analysis chart of the positive electrode active material of Working Example 4-1. Fig. 6 is the discharge performance of the cell of Working Example 1-10. And Fig. 8 is the discharge performance of the cell of Working Example 4-1.

In the figures, 1 is a safety valve, 2 is the lid, 3 is the laser weld zone, 4 is the negative electrode terminal, 5 is the positive electrode terminal, 6 is a gasket, 7 is the positive electrode plate, 8 is the separator, 9 is the negative electrode plate, and 10 is the cell jar.

<Desirable embodiment of the invention>

Embodiments of the present invention are shown below, but the present invention is not limited to these embodiments.

The positive electrode active material of concern in the present invention is a positive electrode active material mainly comprising an Li-Mn-Ni type composite oxide and is characterized by the fact that the specific surface of the aforementioned Li-Mn-Ni composite oxide measured by the BET method (hereinafter referred to as specific surface area, at times) is 0.3 m^2/g or above and 1.5 m^2/g or below. As described above, when the specific surface area is 1.5 m^2/g or below, a nonaqueous secondary cell (hereinafter referred to as cell, at times) having an excellent charge/discharge cycle performance can be produced, and when the specific surface area is 0.3 m^2/g or above, a cell having an excellent high-rate charge/discharge performance can be produced.

[p. 11]

A desirable embodiment of the Li-Mn-Ni type composite oxide of the present invention is explained below. However, the Li-Mn-Ni type composite oxide is not limited to the embodiment shown below.

The first form of the first embodiment of the Li-Mn-Ni type composite oxide is a composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$.

The second form of the first embodiment of Li-Mn-Ni type composite oxide is a composite oxide having a composition in which a part of Mn and Ni that comprise the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ is substituted with a dissimilar element and is indicated by the following general formula:

$$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$$

(Wherein, M is the aforementioned dissimilar element,

$x = 0.001$ to 0.1 ; $x' = 0.001$ to 0.1 ;

$y = 0$ to 0.1 ; $y' = 0$ to 0.1 ;

$x + x' + y + y' \leq 0.4$; $0 \leq z \leq 1$

When $x+x'+y+y' \leq 0.4$, the crystal structure of the composite oxide remains stable despite repeated charge/discharge and excellent charge/discharge cycle performance can be achieved.

The second embodiment of Li-Mn-Ni type composite oxide is a composite oxide having a composition in which a part of Mn and Ni that comprises the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ is replaced with a dissimilar element and is indicated by the following general formula:

[p. 12]

$$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$$

(Wherein, M is the aforementioned dissimilar element,

$x = 0.01$ to 0.1 ; $x' = 0.01$ to 0.1 ;

$y = 0$ to 0.1 ; $y' = 0$ to 0.1 ;

$x + x' + y + y' \leq 0.2$; $0 \leq z \leq 1$

When $x+x'+y+y' \leq 0.2$, the crystal structure of the composite oxide remains stable despite repeated charge/discharge and excellent charge/discharge cycle performance can be achieved.

It is desirable when the above-mentioned dissimilar element M is an element other than Mn, Ni or Li and can be substituted with Mn. For example, B, Be, V, C, Si, P, Sc, Cu, Zn, Ga, Ge, As, Se, Sr, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, Ta, W, Pb, Bi, Co, Fe, Cr, Ni, Ti, Zr, Nb, Y, Al, Na, K, Mg, Ca, Cs, La, Ce, Nd, Sm, Eu, Tb, etc. can be mentioned.

It is further desirable when one of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, or Zn is used for an obvious high-rate discharge performance.

In this case, the x and y that show the substitution ratio of Mn are such that $0<x+y\leq 0.2$, and x' and y' that show the substitution ratio of Ni are such that $0<x'+y'\leq 0.2$. The reason is that the amount of effective lithium decreases when the substitution amount of Mn, x+y, and the substitution amount of Ni, x'+y', are increased.

z represents the amount of lithium used, and the greater the amount of dissimilar element for Mn and Ni, the smaller the ratio.

In this case, the lithium portion indicated by $Li_{y+y'}$ shows the composition ratio in the aforementioned formula, and does not show the arrangement state of the lithium element in the basic skeleton of $LiMn_{0.5}Ni_{0.5}O_2$, or does not show whether it is substituted with a part of the element that comprises the aforementioned basic skeleton.

[p. 13]

The higher the amount of the dissimilar element for Mn and Ni, the higher the high-rate discharge performance at $0<x'+y'\leq 0.2$ and $0<x+y\leq 0.2$, and it is desirable when x and x' are at least 0.001 and at least 0.01, respectively.

The first form of the third embodiment of the Li-Mn-Ni type composite oxide is a composite oxide having a composition in which a part of Mn and Ni that comprise the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ is substituted with a dissimilar element and boron and is indicated by the following general formula:

$$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$$

(Wherein, M' is the aforementioned dissimilar element;

r=0.001 to 0.1 ; r'=0.001 to 0.1 ;

s=0 to 0.1 ; s'=0 to 0.1 ;

$r+r'+s+s'+w+w' \leq 0.4$;

w+w'=0.0005 to 0.01 ; $0 \leq t \leq 1$)

When $r+r'+s+s'+w+w' \leq 0.4$, the crystal structure of the composite oxide remains stable despite repeated charge/discharge, and excellent charge/discharge cycle performance can be achieved.

The second form of the third embodiment of the Li-Mn-Ni type composite oxide is a composite oxide having a composition in which a part of Mn and Ni that comprise the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ is replaced with a dissimilar element and boron and is indicated by the following general formula:

$$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$$

(Wherein, M' is the aforementioned dissimilar element;

r=0.01 to 0.1 ; r'=0.01 to 0.1 ;

s=0 to 0.1 ; s'=0 to 0.1 ;

$r+r'+s+s'+w+w' \leq 0.2$;

w+w'=0.0005 to 0.01 ; $0 \leq t \leq 1$)

[p. 14]

When $r+r'+s+s'+w+w' \leq 0.2$, and the crystal structure of the composite oxide remains stable despite repeated charge/discharge, and excellent charge/discharge cycle performance can be achieved.

Furthermore, in the present specification, the composition of the positive electrode active material containing boron is shown as a dissimilar element where boron is substituted as in the case of

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

but it is known that the aforementioned boron undergoes dissolving by charge/discharge of the cell and is deposited onto the negative electrode. It seems that an active surface is formed on the surface of the crystal particle used as the above-mentioned positive electrode active material when elution of the boron occurs inside the cell where the positive electrode active material itself that utilizes boron as a dissimilar element is used, and as a result, the high-rate discharge performance is improved.

As a means to determine the elemental structure of the particle surface, a method in which measurement were made by X-ray photoelectric spectral analysis (XPS) as etching of the particle is being done can be mentioned. As an example, the change in the concentration of B when etching of the surface of the particle is carried out at a rate of 0.07 nm per second is shown (see Fig. 1 for reference). As shown, in the case of the particle of the sample shown by the black squares, the majority of B is collected at 400 seconds from the surface, that is, approximately 28 μm.

It is desirable for the dissimilar element M' to be an element other than Mn, Ni, or Li and can be substituted for Mn. For example, Be, V, C, Si, P, Sc, Cu, Zn, Ga, Ge, As, Se, Sr, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, Ta, W, Pb, Bi, Co, Fe, Cr, Ni, Ti, Zr, Nb, Y, Al, Na, K, Mg, Ca, Cs, La, Ce, Nd, Sm, Eu, Tb, etc. can be mentioned.

It is further desirable when one of Mg, Al, Ti, V, Cr, Fe, Co, Cu, or Zn is used for an obvious high-rate discharge performance.

In this case, r, s and w that indicate the degree of substitution of Mn are such that $0<r+s+w\leq 0.2$, and r', s' and w' that indicate the degree of substitution of Ni are such that $0<r'+s'+w'\leq 0.2$.

The reason is that when the degree of substitution of Mn $0<r+s+w$ and the degree of substitution of Ni $0<r'+s'+w'$ are increased, the available amount of lithium is reduced.

Furthermore, t represents the amount of lithium available, and the higher the amount of the dissimilar elements for Mn and Ni, the lower the above-mentioned amount.

The greater the amount of the dissimilar elements for Mn and Ni, the higher the degree of increase in high-rate discharge performance when $0<r'+s'+w'\leq 0.2$ and $0<r+s+w\leq 0.2$, and it is desirable when r and r' are at least 0.001, and at least 0.01 is further desirable.

Furthermore, for the method used to replace a part of the aforementioned Mn and Ni with lithium or a dissimilar element in the second embodiment and the third embodiment of the Li-Mn-Ni type composite oxide, a method in which the substituted element is added to the baking raw material of the active material or a method in which baking is performed for $LiMn_{0.5}Ni_{0.5}O_2$, then substitution is performed with the dissimilar element using a method such as an ion-exchange method, etc. can be mentioned, but it is not limited to the above-mentioned methods.

The fourth embodiment of the Li-Mn-Ni type composite oxide is a composite oxide indicated by $Li[Mn_cNi_dCo_eLi_zM''_b]O_2$ (Wherein, M'' is an element other than Mn, Ni, Co and Li, $d\leq c+e+a+b$, $c+d+e+a+b=1$, $0\leq a\leq 0.05$, $0\leq b\leq 0.05$, $0.2\leq c\leq 0.5$, $0.02\leq e\leq 0.4$). When c is 0.2 or below, the cycle performance is likely to be inadequate; on the other hand, when c exceeds 0.5, not only is the cycle performance likely to be inadequate, but also impurities such as Li_2MnO_3 are likely to form stably inside the raw material during the course of baking, starting from a relatively low temperature, and is not desirable. When e exceeds 0.4, thermal stability at the time of charging is likely to be poor. When a exceeds 0.05, discharge capacity is likely to be reduced.

Furthermore, when a study was conducted as the composition ratio of the structural elements was intentionally changed for an improvement in the high-rate charge/discharge performance, to their surprise, a further improvement in the high-rate discharge performance was

possible when a specific dissimilar element was added.

[p. 16]

It is desirable for the dissimilar element M" to be an element other than Mn, Ni, or Li and can be substituted with Mn. For example, B, Be, V, C, Si, P, Sc, Cu, Zn, Ga, Ge, As, Se, Sr, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, Ta, W, Pb, Bi, Fe, Cr, Ni, Ti, Zr, Nb, Y, Al, Na, K, Mg, Ca, Cs, La, Ce, Nd, Sm, Eu, Tb, etc. can be mentioned.

It is further desirable when one of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, or Zn is used for obvious high-rate discharge performance.

The above-mentioned effect achieved cannot be fully explained, but the size of the aforementioned dissimilar element is different from the size of the aforementioned Mn element or Ni element, dissimilar element, is different from the atomic radius of Mn; thus, an influence is placed upon the layer structure of the positive electrode active material, the traveling path of Li ion is influenced, and ion conduction is improved.

Furthermore, the atomic radius, namely, the size, of the aforementioned dissimilar elements other than Mn and Ni vary; thus, it seems that distortion based on expansion and contraction of the active crystal that accompanies charge/discharge is modified as a result of elements with different sizes included.

Furthermore, as a means to include the aforementioned dissimilar elements in the aforementioned composite oxide in the fourth embodiment of the Li-Mn-Ni type composite oxide, a method in which the substituted element is added to the baking raw material ahead of time or a method in which baking is performed; then, substitution with the dissimilar element is achieved using a method such as an ion-exchange method, etc. can be mentioned, but it is not limited to the above-mentioned methods.

Each embodiment of the Li-Mn-Ni type composite oxide is shown absorbed, and the Li-Mn-Ni type composite oxide has peaks at $2\theta=18.6\pm1°$, $36.6\pm1°$, $37.8\pm1°$, $38.2\pm1°$, $44.3\pm1°$, $48.4\pm1°$, $58.4\pm1°$, $64.2\pm1°$, $64.8\pm1°$, $68.8\pm1°$ on the powder X-ray diffraction chart that utilizes

CuKα ray, and good cycle performance can be achieved.

[p. 17]

Furthermore, as described above, it is desirable for the Li-Mn-Ni type composite oxide to have diffraction peaks at 2θ=18.6±1° and at 2θ=44.1±1°, to have the relative intensity ratio of the diffraction peak of 2θ=44.1±1° for the diffraction peak of 2θ=18.6±1° in the range of 0.6 to 1.1, and the half bandwidth of the diffraction peak at 2θ=18.6±1° is in the range of 0.13° to 0.20°, and the half bandwidth of the diffraction peak at 2θ=44.1±1° is in the range of 0.10° to 0.17°.

Furthermore, the lower the particle diameter of the Li-Mn-Ni type composite oxide, the higher the specific surface area and better the output characteristics, but in order to prevent reduction in other properties, especially, storage stability, or taking coatability at the time of production of the electrode into account, it is desirable when the mean particle diameter (D_{50}) is in the range of 3 μm to 30 μm, especially, in the range of 5 μm to 20 μm. When the above-mentioned range is used, the effect on the storage stability and charge/discharge cycle performance of the cell is insignificant, and it is not especially limited. It should be noted that the aforementioned particle diameter is not the particle diameter of the primary particle but the particle diameter of the secondary particle. Furthermore, the mean particle diameter of the positive electrode active material used in working examples shown below is in the range of 9 to 20 μm in all cases.

A suitable method of manufacturing the Li-Mn-Ni type composite oxide is shown below.

It is desirable for the Li-Mn-Ni type composite oxide to have a heat history where baking is done at a temperature of 900°C or above. In specific terms, it is desirable when baking is done "for a Li-Mn-Ni type composite oxide precursor containing at least an Li component, Mn component, and Ni component" at a temperature of 900°C or above to produce a Li-Mn-Ni type composite oxide. In this case, baking temperature in the range of 900°C to 1100°C is desirable, and in the range of 950°C to 1025°C is further desirable.

When the baking temperature is 900°C or below, it is difficult to form the specific surface area of the Li-Mn-Ni type composite oxide at 1.5 m^2/g or below, and a cell with an poor cycle performance is likely to be produced.

On the other hand, when the baking temperature used exceeds 1100°C, the composite oxide with the target composition is less likely to be produced as a result of evaporation of Li, or cell performance is likely to become inferior due to increased density of the particle. When the above-mentioned temperature exceeds 1100°C, an increase in the primary particle growth rate occurs, and the size of the crystal particles of the composite oxide are likely to be increased, and furthermore, localized absence of Li increases and structural instability results.

[p. 18]

It is desirable when the baking time used is in the range of 3 hours to 50 hours. When the baking time exceeds 50 hours, the specific surface area of the Li-Mn-Ni type composite oxide is less likely to become 0.3 m^2/g or greater, and a cell with an inadequate high-rate charge/discharge performance is likely to be produced. On the other hand, when the baking time is 3 hours or less, the specific surface area of the Li-Mn-Ni type composite oxide is less likely to become 1.5 m^2/g or less, and a cell with a poor cycle performance is likely to be produced.

A suitable baking temperature range and suitable baking time are described above, and the conditions are appropriately selected so that the specific surface area of the composite oxide specified in the present invention can be achieved.

Production of Li-Mn-Ni type composite oxide precursor is done via "a method in which an alkali compound is added to an aqueous solution produced by dissolving a manganese (Mn) compound and a nickel (Ni) compound in water, or an aqueous solution produced by dissolving an Mn compound, a Ni compound and a compound containing a dissimilar element (a compound containing the aforementioned dissimilar elements M, M' or M" and is hereinafter referred to as [M] compound at times) in water, and deposition of Mn-Ni composite coprecipitate or Mn-Ni-[M] composite coprecipitate is achieved".

In this case, for the Ni compound, nickel hydroxide, nickel carbonate, nickel sulfate, nickel nitrate, etc., and for Mn compound, manganese oxide, manganese carbonate, manganese sulfate, manganese nitrate, etc. can be mentioned.

For the [M] compound, boric acid, etc. can be used when the dissimilar element is B; vanadium oxide, etc. can be used when the dissimilar element is V; aluminum nitrate, etc. can be used when the dissimilar element is Al; magnesium nitrate, etc. can be used when the dissimilar element is Mg; cobalt hydroxide, cobalt carbonate, cobalt oxide, cobalt sulfate, cobalt nitrate, etc. can be used when the dissimilar element is Co; chromium nitrate, etc. can be used when the dissimilar element is Cr; titanium oxide, etc. can be used when the dissimilar element is Ti; iron sulfate, iron nitrate, etc. can be used when the dissimilar element is Fe; copper sulfate and copper nitrate can be used when the dissimilar element is Cu; and zinc sulfate and zinc nitrate, etc. can be used when the dissimilar element is Zn.

For the alkali compound, ammonium hydroxide, sodium hydroxide, etc. can be mentioned. Furthermore, it is desirable when the alkali compound is used in the form of an aqueous solution.

[p. 19]

When baking is done for a mixture of the Mn-Ni composite coprecipitate or Mn-Ni-[M] composite coprecipitate (hereinafter referred to as "composite coprecipitate" at times) produced as described above and a lithium compound and used as an Li-Mn-Ni type composite oxide precursor according to the above-mentioned baking conditions, production of Li-Mn-Ni type composite oxide can be efficiently achieved.

In this case, for the Li-Mn-Ni type composite oxide precursor, a mixture produced by evaporating water from the aqueous solution of the composite coprecipitate and lithium compound and drying can be used effectively.

For the Li compound, lithium hydroxide, lithium carbonate, etc. can be mentioned.

In addition to the aforementioned main ingredients of the Li-Mn-Ni type composite

oxide, other compounds may be mixed and used in the positive electrode active material of the present invention, and, for example, high cycle performance can be achieved when one or more of the other transition metal oxides containing lithium, etc. is used.

For examples of other transition metal oxide containing lithium, compound indicated by general formula Li_xMX_2, $Li_xMN_yX_2$ (wherein, M and N are metals of groups I to III, X is oxygen or a calcogen compound such as sulfur), and for example, $Li_yCo_{1-x}M_xO_2$, $Li_yMn_{2-x}M_xO_4$ (M is a metal of groups I to III, for example, one or more elements selected from the group consisting of Li, Ca, Cr, Ni, Fe and Co), etc. can be mentioned. As for the value of x that indicates the degree of substitution of the dissimilar element in the aforementioned transition metal oxide containing lithium, the maximum substitution ratio may be used, but from the standpoint of discharge capacity, $0 \leq x \leq 1$ is suitable. Furthermore, the maximum ratio can be used for the value of y that indicates amount of lithium, but from the standpoint of discharge capacity, $0 \leq y \leq 1$ is suitable, but it is not especially limited.

Furthermore, for other compounds, metal compounds such as lithium-cobalt composite oxide and lithium-manganese composite oxide represented by metal compound of group I such as CuO, Cu_2O, Ag_2O, CuS, and $CuSO_4$, metal compound of group IV such as TiS_2, SiO_2, and SnO, metal compound of group V such as V_2O_5, V_6O_{12}, VO_x, Nb_2O_5, $Bi2O_3$, and Sb_2O_3, metal compound of group VI such as CrO_3, Cr_2O_3, MoO_3, MoS_2, WO_3 and SeO_2, metal compound of group VII such as MnO_2, and Mn_2O_3, and metal compound of group VIII such as Fe_2O_3, FeO, Fe_3O_4, Ni_2O_3, NiO, CoO_3, CoO, and furthermore, electrically conductive polymer compounds such as disulfide, polypyrrole, polyaniline, polyparaphenylene, and polyacetylene, carboneous material having pseudo-graphite structure, etc. can be mentioned, but it is not limited to the above-mentioned examples.

[p. 20]

When the aforementioned other compounds are used in combination with the above-mentioned Li-Mn-Ni type composite oxide as a positive electrode active material, the amount of

the other compounds is not especially limited as long as the effect of the present invention is not inhibited, and in general, the amount of the other components is in the range of 1 wt% to 50 wt%, preferably, 5 wt% to 30 wt%, for the total amount of the positive electrode active material.

The nonaqueous secondary cell of the present invention is explained in detail below. The nonaqueous secondary cell (hereinafter referred to as cell, as well) of the present invention is a cell that utilizes the positive electrode active material of the present invention, and in general, comprises the positive electrode mainly consisting of the positive electrode active material of the present invention, negative electrode mainly consisting of the negative material, and a nonaqueous electrolyte in which an electrolytic salt is included in a nonaqueous solvent, and in general, a separator is provided between the positive electrode and negative electrode.

In this case, nonaqueous electrolytes commonly used for lithium cells, etc. may be used. For the nonaqueous solvent, cyclic carbonates such as propylene carbonate, ethylene carbonate, butylene carbonate, chloroethylene carbonate, and vinylene carbonate; cyclic esters such as γ-butylolactone, and γ-valerolactone, chain carbonates such as dimethyl carbonate, diethyl carbonate and ethyl methyl carbonate; chain esters such as methyl formate, methyl acetate, and methyl butyrate, ethers such as 1,3-dioxane, 1,4-dioxane, 1,2-dimethoxy ethane, 1,4-dibuthoxy ethane, and methyl digrime; nitriles such as acetonitrile and benzonitrile; dioxolane and derivatives of the same; ethylene sulfide, sulforane, sultone and derivatives of the same, and mixtures of the same, etc. can be mentioned, but it is not especially limited.

[p. 21]

For electrolytic salts, inorganic ionic salts containing one of lithium (Li), sodium (Na) or potassium (K) such as LiClO4, $LiBF_4$, $LiAsF_6$, $LiPF_6$, LiSCN, LiBr, LiI, Li_2SO_4, $Li_2B_{10}Cl_{10}$, $NaClO_4$, NaI, NaSCN, NaBr, $KClO_4$, KSCN, organic ionic salts such as $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, $LiN(CF_3SO_2)(C_4F_9SO_2)$, $LiC(CF_3SO_2)_3$, $LiC(C_2F_5SO_2)_3$, $(CH_3)_4NBF_4$, $(CH_3)_4NBr$, $(C_2H_5)_4NClO_4$, $(C_2H_5)_4NI$, $(C_3H_7)_4NBr$, (n-$C_4H_9NClO_4$, (n-$C_4H_9)_4NI$, $(C_2H_5)_4N$-maleate, $(C_2H_5)_4N$-benzoate, $(C_2H_5)_4N$-phtalate [sic], lithium stearyl sulfonate, lithium

octyl sulfonate, and lithium dodecyl benzene sulfonate, etc. can be mentioned, and furthermore, one type or two or more different types of the above-mentioned ionic compounds may be mixed and used in combination in this case as well.

Furthermore, the viscosity of the nonaqueous electrolyte can be further reduced when a lithium salt containing perfluoroalkyl group such as $LiBF_4$ and $LiN(C_2F_5SO_2)_2$ is used in combination; thus, low temperature characteristics can be further enhanced.

The concentration of the electrolytic salt in the nonaqueous electrolyte is preferably in the range of 0.1 mol/l to 5 mol/l for production of a cell having high cell performance, and in the range of 1 mol/l to 2.5 mol/l is further desirable.

The electrode structured of the Li-Mn-Ni type composite oxide of the present invention is used as the positive electrode and an electrode structured consisting of graphite is used as the negative electrode in the cell of the present invention.

Production of the positive electrode is achieved as mixing is performed for the composite oxide of the present invention with an electrically conductive material, a binder, and optional filler to form a positive electrode agent, and coating or depositing the positive electrode agent produced onto a foil or lath board used as a collector and heating at a temperature of approximately 50°C to 250°C for 2 hours.

For the negative electrode material, in addition to lithium metal and lithium alloys (alloys containing lithium metals such as lithium-aluminum, lithium-lead, lithium-tin, lithium aluminum-tin, lithium-gallium and wood alloy), alloys capable of occlusion and releasing lithium, carbon materials (for example, graphite, hard carbon, low temperature baked carbon, amorphous carbonate, etc.), etc. can be mentioned. Among those listed above, graphite has an operating potential very close to that of metal lithium; thus, autodischarge can be reduced when a lithium salt is used as an electrolytic salt, and reduction in irreversible capacity at the time of charge/discharge is made possible; thus, it is desirable when used as a negative electrode material.

For example, synthetic graphites and natural graphites can be used effectively. Furthermore, a graphite of which the surface of the negative electrode active material particle is modified with an amorphous carbon is desirable since gas formation at the time of charge/discharge is insignificant.

Analysis result based on Ex-ray analysis, etc. of graphite that can be used effectively in the present invention is shown below.

Lattice spacing (d002): 0.333 to 0.350 nm

Crystal size in a-axis direction La: 20 nm or greater

Crystal size in c-axis direction Lc: 20 nm or greater

True density: 2.00 to 2.25 g/cm^3

Furthermore, metal oxides such as tin oxide and silicon oxide, phosphorus, boron, amorphous carbon, etc. may be added to graphite and modifications can be done as well. When a modification is carried out for the surface of the graphite, decomposition of electrolyte is controlled and cell performance is increased. Furthermore, lithium metals and alloys containing lithium metals such as lithium-aluminum, lithium-lead, lithium-tin, lithium aluminum-tin, lithium-gallium and wood-alloy may be used in combination with graphite, or an electro-chemical reduction may be performed ahead of time so as to include lithium in the graphite, etc. may be used as the negative electrode material as well.

It is desirable for the positive electrode active material fine particle and negative electrode material fine particle to have a mean particle size of 100 μm or below. It is further desirable when the size of the positive electrode active material fine particle is 10 μm or below from the standpoint of increase in the high output performance of the nonaqueous secondary cell. In order to produce fine particles with a specific shape, pulverizers and classifiers are used. For example, mortars, ball mills, sand mills, vibrating ball mills, planetary ball mills, jet mills, counter jet

mills, swivel current jet mills, sieves, etc. are used. In this case, the wet pulverization method, where water or an organic solvent such as hexane is used, may be used. Furthermore, the classification method is not especially limited, and sieves and pneumatic classifiers may be used for wet method or dry method, as needed.

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The positive electrode active material and negative electrode materials used as the primary structural components of positive electrode and negative electrode are explained in detail above, and in addition to the aforementioned primary structural components, electrically conductive materials, binders, thickeners, fillers, etc. may be further included in the aforementioned positive electrode and negative electrode.

The electrically conductive materials used in this case is not especially limited as long as the cell performance is not adversely influenced, and in general, electrically conductive materials such as natural graphites (flaky graphite, scale graphite, earthy graphite, etc.), synthetic graphites, carbon blacks, acetylene blacks, ketchen blacks, carbon whiskers, carbon fibers, metal (copper, nickel, aluminum, silver, gold, etc.) powders, metal fibers, and electrically conductive ceramic materials may be used independently or in combination.

Among electrically conductive materials listed above, acetylene black is further desirable from the standpoint of electron conductivity and coatability. The amount of the electrically conductive material used in this case is preferably in the range of 0.1 wt% to 50 wt%, and in the range of 0.5 wt% to 30 wt% is further desirable. When acetylene black is pulverized to form a super-fine particle of 0.1 to 0.5 μm and used, the amount of carbon required can be reduced. The mixing method used in this case is physical mixing, and uniform mixing is desirable. In this case, wet or dry mixing can be done by using a powder mixer such as V-type mixer, S-type mixer, ball mill, or planetary ball mill.

For the aforementioned binder, in general, thermoplastic resins such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylene and

polypropylene, or polymers with rubber elasticity such as ethylene-propylene-diene terpolymer (EPDM), sulfonated EPDM, styrene butadiene rubber (SBR), and fluoro rubbers may be used independently or in combination. The amount of binder added is in the range of 1 to 50 wt%, preferably, 2 to 30 wt%, for the total weight of the positive electrode or negative electrode.

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In general, for the above-mentioned thickeners, polysacharides such as carboxy methyl cellulose and methyl cellulose may be used independently or in combination. In this case, it is desirable when deactivation, for example, methylation, is performed for the functional group for the thickener having a functional group that forms a reaction with lithium as in the case of polysaccharides. The amount of thickener added is in the range of 0.5 to 10 wt%, preferably, 1 to 2 wt%, for the total weight of the positive electrode or negative electrode.

The filler used in this case is not especially limited as long as the cell performance is adversely influenced. In general, olefin type polymers such as polypropylene and polyethylene, amorphous silica, alumina, zeolite, glass, carbon, etc. are used. The amount of the filler added is 30 wt% or less for the total weight of the positive electrode or negative electrode.

Production of the positive electrode or negative electrode is carried out as an optional electrically conductive material or binder is added to the aforementioned positive electrode active material or positive electrode, mixing is performed with an organic solvent such as N-methylpyrrolidone and toluene, coating the solution produced onto the collector described below and drying the solution. For the coating method used in this case, it is not especially limited and coating can be achieved to form a desired thickness and form using a coating method such as applicator roll coating method, screen coating method, doctor blade coating method, spin coating method, or bar coating method.

For the collector, an electron conductive material with an absence of adverse influence on the cell performance may be used. For example, as a collector for the positive electrode, in addition to materials such as aluminum, titanium, stainless steel, nickel, baked carbon,

conductive polymer, and conductive glass, an aluminum or a copper with the surface treated with a carbon, nickel, titanium or silver for an increase in adhesion, conductivity, and oxidation resistance may be used. As a collector for the negative electrode, in addition to materials such as copper, nickel, iron, stainless steel, aluminum, baked carbon, conductive polymer, conductive glass, and Al-Cd alloy, copper with the surface treated with a carbon, nickel, titanium, or silver for increased adhesion, conductivity, and reduction in resistance may be used. Furthermore, oxidation treatment may be carried out for the surface of the above-mentioned materials as well.

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For the shape of the collector, in addition to foils, films, sheets, nets, punched or expanded materials, lath materials, porous materials, foams, and fibers, etc. may be used. The thickness is not especially limited, and a thickness in the range of 1 to 500 μm is used. Among the above-mentioned collectors, an aluminum foil having high oxidation resistance is desirable for the positive electrode, and an inexpensive copper foil, nickel foil, iron foil and alloy foil containing the same having reduction resistance and electron conductivity are desirable for the negative electrode. Furthermore, a foil with a surface roughness of at least 0.2 μm Ra is desirable, and in this case, high adhesion between the composite coprecipitate or negative electrode and collector can be achieved. Thus, it is desirable when an electrolytic foil having the above-mentioned rough surface is used. In particular, a treated electrolytic foil is further desirable. When both surfaces of the above-mentioned foil are to be coated, it is desirable when each surface roughness of the foil is the same or nearly the same.

It is desirable when a porous film, non-woven fabric, etc. having excellent high-rate discharge performance is used for the separator independently or in combination. For the material that structures the separator, polyolefin type resins such as polyethylene and polypropylene, polyester type resins such as polyethylene terephthalate and polybutylene terephthalate, polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, vinylidene fluoride-perfluorovinyl ether copolymer, vinylidene fluoride-tetrafluoroethylene

copolymer, vinylidene fluoride-trifluoroethylene copolymer, vinylidene fluoride- fluoroethylene copolymer, vinylidene fluoride-hexafluoroacetone copolymer, vinylidene fluoride-ethylene copolymer, vinylidene fluoride-propylene copolymer, vinylidene fluoride-trifluoropropylene copolymer, vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene copolymer, vinylidene fluoride-ethylene-tetrafluoroethylene copolymer, etc. can be mentioned.

From the standpoint of strength, it is desirable when the porosity of the separator is 98 vol% or below. Furthermore, from the standpoint of charge/discharge performance, at least 20 vol% of porosity is desirable.

Furthermore, a polymer gel comprising a polymer such as acrylonitrile, ethylene oxide, propylene oxide, methyl methacrylate, vinyl acetate, vinyl pyrrolidone and polyvinylidene fluoride, and electrolyte may be used as well.

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When the nonaqueous secondary cell of the present invention is used in the form of a gel as described above, it is effective to prevent leakage.

Furthermore, it is desirable when the above-mentioned porous film, non-woven fabric, etc. is used in combination with a polymer gel for the separator since liquid retention of the electrolyte can be improved. In other words, when a polymer having affinity with the solvent is formed on the surface and walls of the micropores of a polyethylene microporous film to form a film with a thickness of several microns or below, and electrolyte is retained inside the aforementioned micropores of the above-mentioned film and production of the aforementioned polymer gel having affinity with solvent can be achieved.

For the aforementioned polymer having affinity with solvent, in addition to polyvinylidene fluoride, acrylate monomers having an ethylene oxide group or ester group, polymers crosslinked with an epoxy monomer or monomers having an isocyanate group, etc. can be mentioned. Crosslinking reaction may be carried out for the above-mentioned monomers by heat-treatment or ultraviolet ray (UV) in the presence of a radical initiator, or by an activated

beam such as an electron beam (EB).

In order to increase the strength and to control properties, modifiers may be included in the aforementioned polymer having affinity with solvent in an amount that does not interfere with the crosslinking property. For examples of the aforementioned modifiers, inorganic fillers [metal oxides such as silicon oxide, titanium oxide, aluminum oxide, magnesium oxide, zirconium oxide, zinc oxide, and iron oxide, metal carbonates such as calcium carbonate and magnesium carbonate], polymers [polyvinylidene fluoride, vinylidene fluoride/hexafluoropropylene copolymer, poly acrylonitrile, polymethyl methacrylate, etc.] etc. can be mentioned. In general, the amount of the aforementioned modifiers added is 50 wt% or below, preferably, 20 wt% or below, for the crosslinking monomer.

For the aforementioned acrylate monomer, unsaturated monomers of bifunctional or higher can be mentioned, and in specific terms, bifunctional (meth)acrylates {ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, adipic acid-dineopentyl glycol ester di(meth)acrylate, polyethylene glycol di(meth)acrylate with polymerization of 2 or higher, polypropylene di(meth)acrylate with polymerization of 2 or higher, di(meth)acrylate of polyoxy ethylene-polyoxy propylene copolymer, butane diol di(meth)acrylate, hexamethylene glycol di(meth)acrylate, etc.},

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trifunctional (meth)acrylates {trimethylol propane tri(meth)acrylate), glycerol tri(meth)acrylate), tri(meth)acrylate) of ethylene oxide adduct of glycerol, tri(meth)acrylate) of propylene oxide adduct of glycerol, ethylene oxide of glycerol, tri(meth)acrylate) of propylene oxide adduct, etc.}, tetrafunctional or higher (meth)acrylates {pentaerythritol tetra (meth)acrylate, diglycerol hexa (meth)acrylate, etc.} can be mentioned. Furthermore, one type or two or more different types of the above-mentioned monomers may be mixed and used in combination in this case.

For the purpose of adjustment of properties, etc., monofunctional monomers may be

added to the aforementioned acrylate monomers. For examples of the aforementioned monofunctional monomers, unsaturated carboxylic acids {acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, vinyl benzoic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, methylene malonic acid, aconitic acid, etc.}, unsaturated sulfonic acids {styrene sulfonate, acrylamide-2-methyl propane sulfonic acid, etc.} or salts of the same (Li salt, Na salt, K salt, ammonium salt, tetraalkyl ammonium salt, etc.), furthermore, a partially esterified above-mentioned unsaturated carboxylic acids with an aliphatic or alicyclic alcohols with C1 to C18, alkylene (C2 to C4) glycol, polyalkylene (C2 to C4) glycol, etc. (methyl maleate, monohydroxy ethyl maleate, etc.) and a partially amidated acids with ammonia, primary or secondary amine (maleic acid monoamide, N-methyl maleic acid monoamide, N,N-diethyl maleic acid monoamide, etc.), (meth)acrylates [esters of C1 to C18 aliphatic alcohols (methyl, ethyl, propyl, butyl, 2-ethyl hexyl, stearyl, etc.) and (meth)acrylic acid, esters of alkylene (C2 to C4) glycol (ethylene glycol, propylene glycol, 1,4-butane diol, etc.) and polyalkylene glycol (C2 to C4) glycol (polyethylene glycol, polypropylene glycol) and (meth)acrylic acid]; (meth)acrylamide or N-substituted (meth)acrylamide [(meth)acrylamide, N-methyl (meth)acrylamide, N-methylol (meth)acrylamide, etc.]; vinyl ester or allyl ester [vinyl acetate, allyl acetate, etc.];

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vinyl ether or allyl ether [butyl vinyl ether, dodecyl allyl ether etc.]; unsaturated nitrile compounds [(meth) acrylonitrile, crotone nitrile, etc.]; unsaturated alcohols [(meth)allyl alcohol, etc.]; unsaturated amines [(meth)allyl amine, dimethyl aminoethyl (meth)acrylate, diethyl aminoethyl (meth)acrylate, etc.]; monomer containing heterocycles [N-vinyl pyrrolidone, vinyl pyridine, etc.]; olefin type aliphatic hydrocarbons [ethylene, propylene, butylene, isobutylene, pentene, (C6 to C50) α-olefin, etc.]; olefin type alicyclic hydrocarbons [cyclopentene, cycrohexene, cycloheptene, norbornane, etc.]; olefin type aromatic hydrocarbons [styrene, α-methyl styrene, stilbene, etc.]; unsaturated imides [maleimide, etc.]; monomers containing halogens [vinyl chloride, vinylidene chloride, vinylidene fluoride, hexafluoropropylene, etc.], etc.

can be mentioned.

For examples of the above-mentioned epoxy monomers, glycidyl ethers {bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, brominated bisphenol A diglycidyl ether, phenol novolak glycidyl ether, diglycidyl ether, cresol novolak glycidyl ether, etc.], glycol esters {hexahydrophthalic acid glycidyl ester, dimer acid glycidyl ester, etc.}, glycidyl amines {triglycidyl isocyanulate, tetraglycidyl diaminophenyl methane, etc.}, linear aliphatic epoxides {epoxidated polybutadiene, epoxidated soybean oil, etc.}, alicyclic epoxides {3,4-epoxy-6-methyl cyclohexyl methyl carboxylate, 3,4-epoxy-cyclohexyl methyl carboxylate, etc.], etc. can be mentioned. The above-mentioned epoxy resins may be used alone or a hardener may be added and curing carried out.

For examples of the aforementioned curing agents, aliphatic polyamines {diethylene triamine, triethylene tetramine, 3,9-(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5,5]undecane, etc.}, aromatic polyamines {metaxylene diamine, diaminophenyl methane, etc.}, polyamides {dimer acid polyamide, etc.}, acid anhydrides {phthalic anhydride, tetrahydromethyl phthalic anhydride, hexahydrophthalic anhydride, trimellitic anhydride, etc.}, phenols {phenol novolak resin, etc.}, polymercaptan {polysulfide, etc.}, tertiary amines {tris(dimethyl aminomethyl) phenol, 2-ethyl-4-methyl imidazole, etc.}, Lewis acid composite complex {trifluoroboron-ethyl amine complex}, etc. can be mentioned.

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For monomers having the aforementioned isocyanate groups, toluene diisocyanate, diphenyl methane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-(2,2,4)-trimethyl-hexamethylene diisocyanate, p-phenylene diisocyanate, 4,4'-dicyclohexyl methane diisocyanate, 3,3'-dimethyl diphenyl-4,4'-diisocyanate, dianicidine diisocyanate, m-xylene diisocyanate, trimethyl xylene diisocyanate, isophorone diisocyanate, 1,5-naphthalene diisocyanate, trans-1,4-cyclohexyl diisocyanate, lysin diisocyanate, etc. can be mentioned.

In crosslinking of the aforementioned isocyanate groups, compounds having active

hydrogen, for example, polyols and polyamines [bifunctional compounds {water, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, etc.}, trifunctional compounds {glycerol, trimethylol propane, 1,2,6-hexane triol, triethanol amine, etc.}, tetrafunctional compounds {pentaerythritol, ethylene diamine, tolylene diamine, diphenyl methane diamine, tetramethylol cyclohexane, methyl glucoxide, etc.}, pentafunctional compounds {2,2,6,6-tetrakis(hydroxy methyl) cyclohexanol, diethylene triamine, etc.}, hexafunctional compounds {sorbitol, mannitol, duicitol, etc.}, octafunctional compounds {succurose, etc.}] and polyether polyols {propylene oxide of the aforementioned polyol or polyamine and/or ethylene oxide adduct}, polyester polyol [a condensate of the aforementioned polyol and polybasic acid {adipic acid, o,m,p-phthalic acid, succinic acid, azelaic acid, sebasic acid, recinoleic acid}, polycaprolactone polyol {poly-epsilon-caprolactone, etc.}, polycondensate of hydroxy carboxylic acid, etc.], etc. may be used in combination.

[p. 30]

Upon performing the above-mentioned crosslinking reaction, a catalyst may be used in combination. For examples of catalysts used in this case, organic tin compounds, trialkyl phosphines, amines, amines [monoamines {N,N-dimethyl cyclohexylamine, triethyl amine, etc.}, cyclic monoamines {pyridine, N-methyl morpholine, etc.}, diamines {N,N,N',N'-tetramethyl ethylene diamine, N,N,N',N'-tetramethyl-1,3-butane diamine, etc.}, triamines {N,N,N',N'-pentamethyl diethylene triamine, etc.}, hexamines {N,N,N',N'-tetra(3-dimethyl aminopropyl)-methane diamine, etc.}, cyclic polyamines {diazabicyclooctane (DABCO), N,N'-dimethyl piperadine, 1,2-dimethyl imidazole, 1,8-diazabicyclo(5,4,0)undecene-7 (DBU), etc.}, and salts of the same] can be mentioned.

Production of the nonaqueous secondary cell concerning the present invention can be achieved when an electrolyte is injected before or after laminating a separator, positive electrode and negative electrode and sealing with a sheath material. Furthermore, in a nonaqueous secondary cell consisting of wrapping a generating component in which the positive electrode

and negative electrode are laminated with the separator in between, it is desirable to inject the electrolyte to the generating component before and after wrapping. As for the injection method used in this case, injection can be performed under ambient pressure, or vacuum impregnation method or pressure impregnation method may be used as well.

For the material used for the sheath of the nonaqueous secondary cell, a nickel-plated iron, stainless steel, aluminum, metal resin composite film, etc. can be mentioned. For example, a metal resin composite film where a metal foil is sandwiched with resin films is desirable. For specific examples of the aforementioned metal foils, foils without pinholes, for example, aluminum, iron, nickel, copper, stainless steel, titanium, gold, and silver, can be used, and a light-weight and low-cost aluminum foil is further desirable in this case. Furthermore, for the resin film used for outside the cell, a resin film having high puncture resistance such as polyethylene terephthalate film and nylon film is desirable, and for the resin film used inside the cell, a thermally-fusible film having high solvent resistance such as polyethylene film and nylon film is desirable.

The structure of the nonaqueous secondary cell is not especially limited, and a coin cell or button cell having a positive electrode, negative electrode and single layer or multilayer separator, furthermore, cylinder cell, square cell, flat cell having a positive electrode, negative electrode and single layer or multilayer separator, etc. can be mentioned.

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<Working examples>

In the following, the present invention is explained further in specific terms with working examples and comparative examples below, but the present invention is not limited to working examples shown below.

[First embodiment]

(Working Example 1-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese

nitrate and nickel nitrate at an atomic ratio for Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was performed to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to a lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was carried out to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated diffraction peaks at around 2θ=18.58 degrees, 36.38 degrees, 37.68 degrees, 38.02 degrees, 44.10 degrees, 48.24 degrees, 58.22 degrees, 63.92 degrees, 64.10 degrees, 64.4 degrees, 67.68 degrees, and a monolayer having high crystallinity that appears to be a layer structure belonging to the spatial group R3/m was synthesized. The X-ray analysis chart of the aforementioned powder is indicated by Fig. 3. As a result of the elemental analysis, the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was defined as Powder A.

The aforementioned Powder A was used as the positive electrode active material, and production of a square nonaqueous secondary cell having a capacity of approximately 15 Ah indicated by Fig. 2 was carried out as shown below.

Mixing was done for Powder A used as the positive electrode active material, acetylene black used as an electrically conductive material, and polyvinylidene fluoride (PVDF) used as a binder at a weight ratio of 85:10:5, N-methyl pyrrolidone was added as a solvent, and kneading and dispersing were carried out to produce a positive electrode coating composition. In this case, a solution with a solid component of the aforementioned polyvinylidene fluoride dispersed in it was used and weight conversion was done for the solid component. The aforementioned positive electrode coating composition was coated onto both surfaces of an aluminum foil collector with a

thickness of 20 μm and an adjustment was made to achieve an overall thickness of 230 μm, and production of a positive electrode sheet having a capacity of 6.3 mAh/cm^2 was achieved. The aforementioned positive electrode sheet was cut to a width of 61 mm and height of 107 mm, and an aluminum lead sheet with a thickness of 20 μm and width of 10 mm was attached to the end of the sheet to form positive electrode plate 7.

[p. 32]

Furthermore, a synthetic graphite (particle diameter 6 μm) was used as a negative electrode material, 10 wt% of polyvinylidene fluoride (PVDF) was added to the aforementioned negative electrode material as a binder, N-methylpyrrolidone was added as a solvent, and kneading and dispersing were done to produce a negative electrode coating composition. In this case, a solution dispersed with a solid component of the aforementioned polyvinylidene fluoride was used and the weight conversion was carried out for the solid component. The aforementioned negative electrode coating composition was coated onto both surfaces of a copper foil collector with a thickness of 10 μm and an adjustment was made to achieve an overall thickness of 180 μm, and production of a negative electrode sheet having a capacity of 7 mAh/cm^2 was achieved. The aforementioned negative electrode sheet was cut to form the width of 65 mm and height of 111 mm, and a copper lead sheet with a thickness of 10 μm and width of 10 mm was attached to the end of the sheet to form negative electrode plate 9.

Vacuum drying was carried out for the aforementioned positive electrode plate 7 and negative electrode plate 9 for 12 hours at a temperature of 150°C. Furthermore, the aforementioned positive electrode plate was inserted into a case with a width of 65 mm and height of 111 mm made of a polyethylene microporous film and used as separator 8, and the positive electrode plate 7 with separator 8 and negative electrode plate 9 were alternatingly laminated to form a laminate consisting of 40 positive electrode plates 7 with separators 8 and 41 negative electrode plates 9.

The aforementioned electrode laminate was wrapped with an insulating film made of a

polyethylene resin, and stored in a square battery jar 10 made of aluminum, the lead plate of positive electrode plate 7 and negative electrode plate 9 are connected with bolts to positive electrode terminal 5 and negative electrode terminal 4, respectively, attached to cover 2 made of aluminum and having safety valve 1. In this case, gasket 6 made of a polypropylene resin was used and terminals 4 and 5 are insulated from the aforementioned cover 2.

Furthermore, welding was performed for the aforementioned cover 2 and battery jar 10 with laser weld 3, 65 g of electrolyte produced by dissolving 1 mol/l of $LiPF_6$ in a 1:1 volume ratio mixed solvent of ethylene carbonate and diethylene carbonate was poured into the aforementioned battery jar 10, and sealing was performed, then, constant-current and constant-voltage charging was done at a temperature of 25°C under 1.5A, 4.2V for 15 hours, and then, constant-current discharge was carried out under 1.5A and at a final voltage of 3V. In this manner, a square lithium cell with a width of 70 mm, height of 130 mm (height with terminal of 136 mm) and depth of 22 mm. The cell produced was defined as the cell of Working Example 1-1.

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(Working Example 1-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed, then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, and stirring was performed, then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particle was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure

similar to that of the above-mentioned powder A. The results of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-2.

(Working Example 1-3)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to a lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1030°C in an oxygen atmosphere, and finally, classification of the particles was done to produce a powder of D_{50}=20 μm. The specific surface area of the particle based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-3.

[p. 34]

(Working Example 1-4)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-

nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1060°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-4.

(Working Example 1-5)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having

a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-5.

(Working Example 1-6)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 950°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

[p. 35]

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-6.

(Working Example 1-7)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was performed to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of

the solvent was done to dry, and baking was done for 12 hours at a temperature of 960°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-7.

(Working Example 1-8)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was performed to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 980°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell

having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-8.

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(Working Example 1-9)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was performed to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 5 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particle based on the BET method was 0.3 m^2/g.

The measurement result of the X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-9.

(Working Example 1-10)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent

was done to dry, and baking was done for 5 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.3 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The X-ray diffraction chart of the aforementioned powder is indicated by Fig. 4. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-10.

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(Working Example 1-11)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 20 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=5 μm. The specific surface area of the particles based on the BET method was 1.5 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The X-ray diffraction chart of the aforementioned powder is indicated by Fig. 4. The result of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above

was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 1-11.

(Comparative Example 1-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1.9:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 3 hours at a temperature of 950°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.6 m^2/g.

Based on the results of X-ray analysis of the above-mentioned powder by CuKα ray, diffraction peaks were observed at 2θ 18 degrees, 37 degrees, 39 degrees, 45 degrees, 61 degrees, 65 degrees and 67 degrees, and synthesis of layer-structured halite that belongs to special group C3/m was confirmed. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.95}Ni_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 1-1.

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(Comparative Example 1-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and precipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese compound. The aforementioned manganese compound

was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 3 hours at a temperature of 850°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=10 μm. The specific surface area of the particles based on the BET method was 0.4 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a crystal having a spinel structure. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{1.05}Ni_{1.95}O_4$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 1-2.

(Comparative Example 1-3)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 3 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=3 μm. The specific surface area of the particles based on the BET method was 2.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 1-3.

(Comparative Example 1-4)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 15 hours at a temperature of 800°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=5 μm. The specific surface area of the particles based on the BET method was 2.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 1-4.

(Comparative Example 1-5)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 24 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=5 μm. The specific surface area of the particles based on the BET method was 0.2 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of the elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 1-5.

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(Comparative Example 1-6)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 1:1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. The aforementioned manganese-nickel coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 24 hours at a temperature of 1100°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=30 μm. The specific surface area of the particles based on the BET method was 0.2 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.5}Ni_{0.5}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 1-6.

[Second embodiment]

(Working Example 2-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 0.95:0.95 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel coprecipitate compound. Furthermore, the aforementioned manganese-nickel coprecipitate compound and boric acid were added to lithium hydroxide solution at an elemental ratio of Li:Mn:Ni:B of 2:0.95:0.95:0.10, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-1.

(Working Example 2-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and vanadium oxide at an atomic ratio of Mn:Ni:V of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-vanadium coprecipitate compound.

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Furthermore, the aforementioned manganese-nickel-vanadium coprecipitate compound was added to lithium hydroxide solution, then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific

surface area of the particles based on the BET method was 0.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}V_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-2.

(Working Example 2-3)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and aluminum nitrate at an atomic ratio of Mn:Ni:Al of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-aluminum coprecipitate compound. Furthermore, the aforementioned manganese-nickel-aluminum coprecipitate compound was added to lithium hydroxide solution; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Al_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-3.

(Working Example 2-4)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and magnesium nitrate at an atomic ratio of Mn:Ni:Mg of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-magnesium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-magnesium coprecipitate compound was added to lithium hydroxide solution; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

[p. 42]

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-4.

(Working Example 2-5)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned manganese-nickel-cobalt coprecipitate compound was added to lithium hydroxide solution; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the

particles based on the BET method was 0.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Co_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-5.

(Working Example 2-6)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and chromium nitrate at an atomic ratio of Mn:Ni:Cr of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-chromium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-magnesium coprecipitate compound was added to lithium hydroxide solution; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

[p. 43]

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Cr_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-6.

(Working Example 2-7)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, and titanium oxide at an atomic ratio of Mn:Ni:Ti of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-vanadium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-titanium coprecipitate compound was added to lithium hydroxide solution; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Ti_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-7.

(Working Example 2-8)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and iron sulfate at an atomic ratio of Mn:Ni:Fe of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-iron coprecipitate compound. Furthermore, the aforementioned manganese-nickel-iron coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of

the particles based on the BET method was 0.9 m^2/g.

[p. 44]

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Fe_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-8.

(Working Example 2-9)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and copper sulfate at an atomic ratio of Mn:Ni:Cu of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-copper coprecipitate compound. Furthermore, the aforementioned manganese-nickel-copper coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Cu_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-9.

(Working Example 2-10)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and zinc sulfate at an atomic ratio of Mn:Ni:Zn of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-zinc coprecipitate compound. Furthermore, the aforementioned manganese-nickel-zinc coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A.

[p. 45]

The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Zn_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 2-10.

(Comparative Example 2-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and magnesium nitrate at an atomic ratio of Mn:Ni:Mg of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-magnesium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-magnesium coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and

baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=15 μm. The specific surface area of the particles based on the BET method was 0.2 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 2-1.

(Comparative Example 2-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and magnesium nitrate at an atomic ratio of Mn:Ni:Mg of 0.95:0.95:0.1 and coprecipitation was performed; then, heating was provided to 150°C and sequentially, drying was done to produce a manganese-nickel-magnesium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-magnesium coprecipitate compound was added to lithium hydroxide solution, stirring was provided; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=6 μm. The specific surface area of the particles based on the BET method was 1.9 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be the layer structure similar to that of the above-mentioned powder A.

[p. 46]

The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$. The powder produced above was used as the positive electrode

active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 2-2.

[Third embodiment]

(Working Example 3-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 0.95:0.95 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was performed to produce a manganese-nickel coprecipitate compound. Furthermore, the aforementioned manganese-nickel coprecipitate compound and boric acid were added to lithium hydroxide solution at an elemental ratio Li:Mn:Ni:B of 2.00:0.95:0.95:0.1; then, baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The above-mentioned powder produced was defined as powder B. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$.

Segregation of the B (boron) on the surface was observed when an analysis was made in the depth direction (see Fig. 1 for reference). The powder B produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 3-1.

(Working Example 3-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese

nitrate, nickel nitrate, and vanadium oxide at an atomic ratio of Mn:Ni:V of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-vanadium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-vanadium coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:V:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm.

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The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}V_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-2.

(Working Example 3-3)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, and aluminum nitrate at an atomic ratio of Mn:Ni:Al of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel- aluminum coprecipitate compound. Furthermore, the aforementioned manganese-nickel-aluminum coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Al:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an

oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Al_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-3.

(Working Example 3-4)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and magnesium nitrate at an atomic ratio of Mn:Ni:Mg of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-magnesium coprecipitate compound.

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Furthermore, the aforementioned manganese-nickel-magnesium coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Mg:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Mg_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-4.

(Working Example 3-5)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned manganese-nickel-cobalt coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Co:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Co_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-5.

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(Working Example 3-6)

A sodium hydroxide solution was added to an aqueous solution containing manganese

nitrate, nickel nitrate and chromium nitrate at an atomic ratio of Mn:Ni:Cr of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-vanadium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-chromium coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Cr:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Cr_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-6.

(Working Example 3-7)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, and titanium oxide at an atomic ratio of Mn:Ni:V of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel- titanium coprecipitate compound. Furthermore, the aforementioned manganese-nickel-titanium coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Ti:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was

1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Ti_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-7.

[p. 50]

(Working Example 3-8)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, and iron sulfate at an atomic ratio of Mn:Ni:Fe of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-iron coprecipitate compound. Furthermore, the aforementioned manganese-nickel-iron coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Fe:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Fe_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2

was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-8.

(Working Example 3-9)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and copper sulfate at an atomic ratio of Mn:Ni:Cu of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-copper coprecipitate compound. Furthermore, the aforementioned manganese-nickel-copper coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Cu:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Cu_{0.05}B_{0.001}O_2$.

[p. 51]

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-9.

(Working Example 3-10)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, and zinc sulfate at an atomic ratio of Mn:Ni:Zn of 0.95:0.948:0.1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying

was done to produce a manganese-nickel-zinc coprecipitate compound. Furthermore, the aforementioned manganese-nickel-zinc coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Zn:B of 2:0.95:0.948:0.1:0.002, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=10 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g. The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.474}Zn_{0.05}B_{0.001}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 3-10.

(Comparative Example 3-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 0.95:0.95 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel coprecipitate compound. Furthermore, the aforementioned manganese-nickel coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:B of 2.00:0.95:0.95:0.1, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.2 m^2/g.

[p. 52]

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 3-1.

(Comparative Example 3-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate and nickel nitrate at an atomic ratio of Mn:Ni of 0.95:0.95 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel coprecipitate compound. Furthermore, the aforementioned manganese-nickel coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:B of 2.00:0.95:0.95:0.1, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=4 μm. The specific surface area of the particles based on the BET method was 2.4 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder A. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 3-2.

[Fourth embodiment]

(Working Example 4-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 9:9:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. The aforementioned manganese-nickel-cobalt coprecipitate compound was added to lithium hydroxide solution, stirring was performed; then, evaporation of the solvent was done to dry, and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

[p. 53]

Based on the results of X-ray analysis of the above-mentioned powder by CuKα ray, diffraction peaks were observed at 2θ 18.56 degrees, 36.56 degrees, 38.24 degrees, 44.32 degrees, 48.4 degrees, 58.4 degrees, 64.16 degrees, 64.8 degrees, and 68.8 degrees, and a monolayer having high crystallinity that appears to be a layer structure that belongs to spatial group R3m was synthesized. The X-ray diffraction chart of the aforementioned powder is indicated by Fig. 5. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$. The above-mentioned powder produced was defined as powder D.

The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-1.

(Working Example 4-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 2:2:1 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned manganese-nickel-cobalt coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-2.

[p. 54]

(Working Example 4-3)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 9:9:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned manganese-nickel-cobalt coprecipitate compound was added to lithium hydroxide solution and baking was done for 5 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 0.3 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray

indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-3.

(Working Example 4-4)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 9:9:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned manganese-nickel-cobalt coprecipitate compound was added to lithium hydroxide solution and baking was done for 20 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=5 μm. The specific surface area of the particles based on the BET method was 1.5 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-4.

(Working Example 4-5)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 17:17:4 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying

was done to produce a manganese-nickel-cobalt coprecipitate compound.

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Furthermore, the aforementioned coprecipitate compound and boric acid were added to lithium hydroxide solution to form an elemental ratio of Li:Mn:Ni:Co:B of 2:0.85:0.85:0.2:0.1 and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}B_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-5.

(Working Example 4-6)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate and vanadium oxide at an atomic ratio of Mn:Ni:Co:V of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt-vanadium coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that

the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}V_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-6.

(Working Example 4-7)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate and aluminum nitrate at an atomic ratio of Mn:Ni:Co:Al of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt-aluminum coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}Al_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-7.

(Working Example 4-8)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate and magnesium nitrate at an atomic ratio of Mn:Ni:Co:Mg of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt-magnesium coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium

hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}Mg_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-8.

[p. 57]

(Working Example 4-9)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate, and chromium nitrate at an atomic ratio of Mn:Ni:Co:Cr of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt-chromium coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}Cr_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in

(Working Example 1-1). The cell produced was defined as the cell of Working Example 4-9.

(Working Example 4-10)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate and titanium oxide at an atomic ratio of Mn:Ni:Co:Ti of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt- titanium coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 1.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}Ti_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-10.

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(Working Example 4-11)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate and iron sulfate at an atomic ratio of Mn:Ni:Co:Fe of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt-iron coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of

D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}Fe_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-11.

(Working Example 4-12)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate, and copper sulfate at an atomic ratio of Mn:Ni:Co:Cu of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt-copper coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}Cu_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-12.

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(Working Example 4-13)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, cobalt nitrate, and zinc sulfate at an atomic ratio of Mn:Ni:Co:Zn of 17:17:4:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt-zinc coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=9 μm. The specific surface area of the particles based on the BET method was 0.9 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.425}Ni_{0.425}Co_{0.1}Zn_{0.05}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Working Example 4-13.

(Comparative Example 4-1)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 7:11:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 12 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=20 μm. The specific surface area of the particles based on the BET method was 20 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure

similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.35}Ni_{0.55}Co_{0.1}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 4-1.

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(Comparative Example 4-2)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 9:9:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 24 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=5 μm. The specific surface area of the particles based on the BET method was 0.3 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 4-2.

(Comparative Example 4-3)

A sodium hydroxide solution was added to an aqueous solution containing manganese nitrate, nickel nitrate, and cobalt nitrate at an atomic ratio of Mn:Ni:Co of 9:9:2 and coprecipitation was performed; then, heating was provided to 150°C and subsequently, drying

was done to produce a manganese-nickel-cobalt coprecipitate compound. Furthermore, the aforementioned coprecipitate compound was added to lithium hydroxide solution and baking was done for 3 hours at a temperature of 1000°C in an oxygen atmosphere, and finally, classification of the particles was carried out to produce a powder of D_{50}=5 μm. The specific surface area of the particles based on the BET method was 2.0 m^2/g.

The measurement results of X-ray analysis of the above-mentioned powder by CuKα ray indicated formation of a monolayer having high crystallinity that appears to be a layer structure similar to that of the above-mentioned powder D. The results of elemental analysis indicated that the composition of the aforementioned powder was $LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$. The powder produced above was used as the positive electrode active material and production of a square lithium cell having a capacity of approximately 15 Ah indicated by Fig. 2 was done as in (Working Example 1-1). The cell produced was defined as the cell of Comparative Example 4-3.

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(Cell performance test)

A High-rate discharge performance test was performed for the above-mentioned cells of the present invention and cells of comparisons at a temperature of 25°C, and subsequently, charge/discharge cycle performance was tested as well.

As for the condition used for the high-rate discharge performance test, charging was performed at constant-current 7.5 A (0.5It), 4.3 V, and 3 hrs, and discharging was done at constant-current 1.5 A (0.1It), 30 V (2It), end voltage of 3.0V.

For the condition used for the charge/discharge cycle test, charging was done at constant-current 7.5 A (0.5It), 4.3 V, and 3 hrs, and discharging was done at constant-current 7.5 A (0.5It) and end voltage of 3.0V. 10 minutes dead time mode was provided after charging and discharging.

In the high-rate discharge performance test, the ratio of the discharge capacity when discharging is done at 1.5 A for the discharge capacity when discharging is done at 30 A is

defined as high-rate discharge performance (%). In the charge/discharge cycle performance test, the number of cycles where the discharge capacity is reduced to 80% of the initial discharge capacity is defined as the cycle life. The results of the above-mentioned performance tests are indicated by Table I to Table IV below. In the Tables, "half bandwidth 18.6°" means the half bandwidth of the diffraction peak at $2\theta=18.6\pm1°$, and "half bandwidth 44.1°" means the half bandwidth of the diffraction peak at $2\theta=44.1\pm1°$, and furthermore, "peak intensity ratio" means the relative peak intensity ratio at the diffraction peak at $2\theta=44.1\pm1°$ for the diffraction peak at $2\theta=18.6\pm1°$.

Table I [p. 62] BW* = Bandwidth

Cell	Positive electrode active material						Cell performance			
	Composition	Specific surface area (g/m^2)	Mean particle diameter (μm)	Peak intensity ratio	Half BW* 18.6°	Half BW* 44.1°	1.5 A discharge capacity (mAh/g)	30 A discharge capacity (mAh/g)	High-rate discharge perf. (%)	Cycle life
Work. Ex. 1-1	$LiMn_{0.5}Ni_{0.5}O_2$	1.5	9	1.0	0.17	0.15	140	85	60.7	500
Work. Ex. 1-2	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	0.9	0.17	0.14	140	85	60.7	500
Work. Ex. 1-3	$LiMn_{0.5}Ni_{0.5}O_2$	2.0	20	0.6	0.20	0.17	150	92	61.3	350
Work. Ex. 1-4	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	0.6	0.17	0.15	150	93	62.0	450
Work. Ex. 1-5	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	1.1	0.17	0.12	118	81	60.0	480
Work. Ex. 1-6	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	1.1	0.13	0.12	135	78	57.8	520
Work. Ex. 1-7	$LiMn_{0.5}Ni_{0.5}O_2$	1.5	20	1.2	0.17	0.12	130	65	50.0	550
Work. Ex. 1-8	$LiMn_{0.5}Ni_{0.5}O_2$	0.9	20	1.0	0.12	0.10	137	62	45.3	500
Work. Ex. 1-9	$LiMn_{0.5}Ni_{0.5}O_2$	0.3	20	0.9	0.18	0.15	140	84	60.0	510
Work. Ex. 1-10	$LiMn_{0.5}Ni_{0.5}O_2$	0.3	9	0.9	0.17	0.15	140	84	60.0	510
Work. Ex. 1-11	$LiMn_{0.5}Ni_{0.5}O_2$	1.5	5	0.9	0.17	0.15	140	85	60.7	470
Comp. Ex. 1-1	$LiMn_{0.95}Ni_{0.05}O_2$	0.9	20	0.6	0.20	0.12	150	50	31.3	300
Comp. Ex. 1-2	$Li_{1.05}Mn_{1.95}O_4$	0.4	10	0.7	0.17	0.12	118	90	76.3	350
Comp. Ex. 1-3	$LiMn_{0.5}Ni_{0.5}O_2$	2.0	3	0.9	0.17	0.17	140	87	62.1	250
Comp. Ex. 1-4	$LiMn_{0.5}Ni_{0.5}O_2$	2.0	5	0.4	0.21	0.18	110	70	63.6	250
Comp. Ex. 1-5	$LiMn_{0.5}Ni_{0.5}O_2$	0.2	5	0.9	0.19	0.16	140	87	62.1	250
Comp. Ex. 1-6	$LiMn_{0.5}Ni_{0.5}O_2$	0.2	30	0.9	0.12	0.10	120	72	60.0	480

Table II

Cell	Positive electrode active material						Cell performance			
	Composition	Specific surface area (g/m^2)	Mean particle diameter (μm)	Peak intensity ratio	Half BW* 18.6°	Half BW* 44.1°	1.5 A discharge capacity (mAh/g)	30 A discharge capacity (mAh/g)	High-rate discharge perf. (%)	Cycle life
Work. Ex. 2-1	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	0.9	9	0.9	0.16	0.16	137	89	65.0	350
Work. Ex. 2-2	$LiMn_{0.475}Ni_{0.475}V_{0.05}O_2$	0.9	9	0.9	0.17	0.17	130	87	66.9	350
Work. Ex. 2-3	$LiMn_{0.475}Ni_{0.475}Al_{0.05}O_2$	0.9	9	1.0	0.16	0.11	128	89	69.0	350
Work. Ex. 2-4	$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$	1.0	9	1.0	0.16	0.17	132	89	67.4	350
Work. Ex. 2-5	$LiMn_{0.475}Ni_{0.475}Co_{0.05}O_2$	0.9	9	1.0	0.14	0.14	128	88	68.8	350
Work. Ex. 2-6	$LiMn_{0.475}Ni_{0.475}Cr_{0.05}O_2$	0.9	9	0.9	0.17	0.17	128	84	65.6	350
Work. Ex. 2-7	$LiMn_{0.475}Ni_{0.475}Ti_{0.05}O_2$	0.9	9	0.9	0.16	0.17	129	87	67.4	350
Work. Ex. 2-8	$LiMn_{0.475}Ni_{0.475}Fe_{0.05}O_2$	0.9	9	0.9	0.16	0.13	128	85	66.4	350
Work. Ex. 2-9	$LiMn_{0.475}Ni_{0.475}Cu_{0.05}O_2$	0.9	9	0.9	0.16	0.14	127	83	65.4	350
Work. Ex. 2-10	$LiMn_{0.475}Ni_{0.475}Zn_{0.05}O_2$	0.9	9	0.9	0.17	0.13	128	84	65.6	350
Comp. Ex. 2-1	$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$	0.2	15	1.1	0.17	0.17	95	40	42.1	300
Comp. Ex. 2-2	$LiMn_{0.475}Ni_{0.475}Mg_{0.05}O_2$	1.9	6	1.1	0.16	0.16	130	90	69.2	150

*BW = Bandwidth

Table III

Cell	Positive electrode active material						Cell performance			
	Composition	Specific surface area (g/m^2)	Mean particle diameter (μm)	Peak intensity ratio	Half BW* 18.6°	Half BW* 44.1°	1.5 A discharge capacity (mAh/g)	30 A discharge capacity (mAh/g)	High-rate discharge perf. (%)	Cycle life
Work. Ex. 3-1	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	1.0	9	1.0	0.15	0.12	137	89	65.0	600
Work. Ex. 3-2	$LiMn_{0.475}Ni_{0.474}V_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.14	0.11	130	90	69.2	550
Work. Ex. 3-3	$LiMn_{0.475}Ni_{0.474}Al_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.13	0.11	129	92	71.3	600
Work. Ex. 3-4	$LiMn_{0.475}Ni_{0.474}Mg_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.13	0.13	132	92	69.7	650
Work. Ex. 3-5	$LiMn_{0.475}Ni_{0.474}Co_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.13	0.11	131	90	71.0	700
Work. Ex. 3-6	$LiMn_{0.475}Ni_{0.474}Cr_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.14	0.11	128	87	68.0	650
Work. Ex. 3-7	$LiMn_{0.475}Ni_{0.474}Ti_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.16	0.14	129	90	69.8	500
Work. Ex. 3-8	$LiMn_{0.475}Ni_{0.474}Fe_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.16	0.14	125	86	68.8	480
Work. Ex. 3-9	$LiMn_{0.475}Ni_{0.474}Cu_{0.05}B_{0.001}O_2$	1.0	9	1.0	0.15	0.13	127	90	66.9	500
Work. Ex. 3-10	$LiMn_{0.475}Ni_{0.474}Zn_{0.05}B_{0.001}O_2$	1.0	10	1.0	0.16	0.15	130	90	71.5	510
Comp. Ex. 3-1	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	0.2	9	1.1	0.15	0.23	110	70	63.6	470
Comp. Ex. 3-2	$LiMn_{0.475}Ni_{0.475}B_{0.05}O_2$	2.4	4	1.1	0.17	0.21	132	90	72.0	200

*BW = Bandwidth

Table IV [p. 65] BW* = Bandwidth

Cell	Positive electrode active material						Cell performance			
	Composition	Specific surface area (g/m^2)	Mean particle diameter (μm)	Peak intensity ratio	Half BW* 18.6°	Half BW* 44.1°	1.5 A discharge capacity (mAh/g)	30 A discharge capacity (mAh/g)	High-rate discharge perf. (%)	Cycle life
Work. Ex. 4-1	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	1.0	20	1.0	0.19	0.12	160	113	70.6	700
Work. Ex. 4-2	$LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$	0.9	20	1.0	0.19	0.11	165	120	72.7	750
Work. Ex. 4-3	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	0.3	20	1.0	0.15	0.14	160	112	70.0	600
Work. Ex. 4-4	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	1.0	5	1.0	0.19	0.10	160	112	71.3	700
Comp. Ex. 4-1	$LiMn_{0.35}Ni_{0.55}Co_{0.1}O_2$	1.0	20	1.0	0.18	0.13	160	115	75.0	400
Comp. Ex. 4-2	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	0.3	5	1.0	0.20	0.10	160	94	58.8	300
Comp. Ex. 4-3	$LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$	2.0	5	0.5	0.07	0.02	160	120	75.0	350
Work. Ex. 4-5	$LiMn_{0.425}Ni_{0.425}Co_{0.1}B_{0.05}O_2$	1.0	9	1.0	0.18	0.14	157	118	75.2	700
Work. Ex. 4-6	$LiMn_{0.425}Ni_{0.425}Co_{0.1}V_{0.05}O_2$	1.0	9	0.9	0.19	0.02	150	111	78.4	600
Work. Ex. 4-7	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Al_{0.05}O_2$	1.0	9	1.0	0.15	0.13	155	113	78.9	700
Work. Ex. 4-8	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Mg_{0.05}O_2$	1.0	9	1.0	0.19	0.13	152	114	75.0	700
Work. Ex. 4-9	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Cr_{0.05}O_2$	1.0	9	1.0	0.19	0.14	152	114	78.0	650
Work. Ex. 4-10	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Ti_{0.05}O_2$	1.0	9	1.0	0.19	0.15	154	112	72.7	650
Work. Ex. 4-11	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Fe_{0.05}O_2$	0.3	9	0.9	0.19	0.11	150	115	72.7	650
Work. Ex. 4-12	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Cu_{0.05}O_2$	0.3	9	1.0	0.20	0.10	151	115	76.2	620
Work. Ex. 4-13	$LiMn_{0.425}Ni_{0.425}Co_{0.1}Zn_{0.05}O_2$	0.3	9	1.0	0.19	0.12	153	120	78.4	650

Furthermore, the change in the discharge voltage of the cell of (Working Example 1-1) when discharging is done at 1.5 A (0.1It) is indicated by Fig. 6, the change in the discharge voltage of the cell of (Working Example 1-10) when discharging is done at 1.5 A (0.1It) is indicated by Fig. 7, and the change in the discharge voltage of the cell of (Working Example 4-1) when discharging is done at 1.5 A (0.1It) is indicated by Fig. 8, respectively.

(Regarding the first embodiment)

When comparison is made between the cells of (Working Example 1-1) to (Working Example 1-11) that utilize the positive electrode active material having the layer structure belonging to spatial group R3/m and the cell of (Comparative Example 1-1) that utilizes the positive electrode active material having the layer structure belonging to spatial group C2/m, a significant increase in the high-rate discharge performance is observed. Furthermore, when comparison is made among cells that utilize a positive electrode active material $LiMn_{0.5}Ni_{0.5}O_2$ having a layer similar to the space group R3/m of (Working Example 1-1) to (Working Example 1-11) and (Comparative Example 1-3) to (Comparative Example 1-6), an obvious improvement in the high-rate discharge performance is observed when the value of the specific surface area is at least 0.3 m^2/g. On the other hand, a sharp decrease in the charge/discharge cycle is observed when the value of the aforementioned specific surface area exceeds 1.5 m^2/g. Therefore, when an $LiMn_{0.5}Ni_{0.5}O_2$ having a specific surface area in the range of 0.3 m^2/g to 1.5 m^2/g is used as a positive electrode active material, production of a secondary cell having excellent cycle performance and high-rate discharge performance is made possible.

Furthermore, when a composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ is used and a comparison is made on cell performance of cells having different relative intensity ratios of the diffraction peak at $2\theta=44.1\pm1°$ for the diffraction peak of $2\theta=18.6\pm1°$ on the powder X-ray diffraction chart that utilizes CuKα ray, a significant increase in the cycle life is observed when the relative intensity ratio exceeds 0.6. Furthermore, reduction in the high-rate discharge

performance is observed when the aforementioned relative intensity ratio exceeds 1.1. Thus, when the aforementioned relative intensity ratio is between 0.6 to 1.1, production of cells with excellent cycle life and high-rate discharge performance is made possible.

Furthermore, when the half bandwidth is 0.13° or above at 2θ=18.6±1° and the half bandwidth is 0.10° or above at 2θ=44.1±1°, excellent high-rate discharge performance can be achieved.

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Furthermore, when the half bandwidth is 0.20° or above at 2θ=18.6±1° and at the same time, the half bandwidth is 0.17° or above at 2θ=44.1±1°, reduction in cycle life is observed. Thus, production of a cell having an excellent cycle life and high-rate discharge performance is made possible when the half bandwidth is in the range of 0.13 to 0.20° at 2θ=18.6±1° and at the same time, the half bandwidth is 0.10 to 0.17° at 2θ=44.1±1°.

It should be noted that the cell of (Comparative Example 1-2) having a relatively good high-rate discharge performance utilizes spinel manganese as the active material of positive electrode. In the above-mentioned cell, the expected high-rate discharge performance is achieved by spinel manganese, which indicates that the rate-determining factor of the discharge performance is not based on electrolyte or negative electrode, which are the structural elements other than positive electrode in the working examples and comparative examples.

(Regarding the second embodiment)

When the cells of (Working Example 2-1) to (Working Example 2-7) in which a part of the Mn and Ni that comprise the $LiMn_{0.5}Ni_{0.5}O_2$ is replaced with a dissimilar element, a significant increase in the value of the high-rate discharge performance is observed in comparison to the cell made of a positive electrode active material having similar properties. The above-mentioned effect achieved is not well understood, but it seems that increase in shifting of the lithium ion occurs when some of the Ni and Mn is replaced with a small amount of another element.

Furthermore, the value of the high-rate discharge performance is insufficient in a cell where the value of the specific surface area is less than 0.3 m^2/g (Comparative Example 2-1) in the second embodiment. On the other hand, in a cell where the value of specific surface area exceeds 1.5 m^2/g (comparative Example 2-2), a sharp decrease in the charge/discharge cycle is observed.

(Regarding the third embodiment)

Furthermore, compared with cells of (Working Example 1-1) to (Working Example 1-11), the high-rate discharge performance is high in the cell of (Working Example 3-1) and the effect achieved through substitution of boron is observed.

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In cells of (Working Example 3-2) to (Working Example 3-7) in which a part of the Mn and Ni in $LiMn_{0.5}Ni_{0.5}O_2$ is replaced with boron and other elements, a further improvement in the high-rate discharge performance is observed. It is hypothesized that an increase in shifting of the lithium ion occurs when the Ni and Mn are replaced with a small amount of other elements.

Furthermore, the value of the high-rate discharge performance is insufficient in a cell where the value of the specific surface area is less than 0.3 m^2/g (comparative Example 3-1) in the third embodiment. On the other hand, in a cell where the value of specific surface area exceeds 1.5 m^2/g (Comparative Example 3-2), a sharp decrease in the charge/discharge cycle is observed.

Furthermore, as indicated by Fig. 1, when the etching time based on the X-ray photoelectron spectra method (XPS) is approximately 400 seconds, the concentration of the boron is reduced to approximately the same as inside the particle. In this case, the etching rate in the depth direction is 0.07 nm (sec). This indicates that the thickness of the surface layer of the positive electrode active material particle required to achieved the effect of the present invention is 28 nm (=0.028 μm) at most. When the mean particle diameter of the positive electrode active material is 9 to 10 μm, the aforementioned thickness corresponds to approximately 2% of the

diameter.

(Regarding the fourth embodiment)

Furthermore, in cells where the composite oxide indicated by $Li[Mn_xNi_yCo_z]O_2$ where a Co component is added to a composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ (Working Example 4-1) to (Working Example 4-4), a significant increase in discharge capacity is observed in comparison to the cells of (Working Example 1-1) to (Working Example 1-11). Furthermore, possibly due to stable crystal structure, a significant increase in cycle life is observed.

When comparison is made for the cell performance among composite oxides in which the same structural formula of $LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$ is used as positive electrode active material but the specific surface area is different (Working Example 4-1), (Working Example 4-3), (Working Example 4-4), (Comparative Example 4-2) and (Comparative Example 4-3), a sharp decrease in cycle performance is observed when the specific surface area exceeds 1.5 m^2/g. Furthermore, a sharp decrease in high-rate discharge performance is observed when the specific surface area becomes less than 0.3 m^2/g. Thus, a nonaqueous secondary cell equipped with excellent cycle performance and excellent high-rate discharge performance can be produced when the value of the specific surface area of the composite oxide is in the range of 0.3 m^2/g to 1.5 m^2/g.

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An increased value of the high-rate discharge performance is observed in cells in which the composite oxide indicated by the structural formula of $LiMn_{0.425}Ni_{0.425}Co_{0.1}M_{0.05}O_2$ where a dissimilar element M" is added to Ni, Mn, and Co is used as a positive electrode active material (Working Example 4-5) to (Working Example 4-10) in comparison to the cell without a dissimilar element M" (Working Example 4-1). The above-mentioned effect achieved is not well understood, but it seems that increase in shifting of the lithium ion occurs when the Ni and Mn are replaced with a small amount of other elements.

Furthermore, when disassembly is performed for the cells of Working Example 2-1, Working Example 3-1, and Working Example 4-7 with boron added and an elemental analysis

was performed for each structural element that comprises the cell, boron was detected at near the surface of the negative electrode. Based on the result obtained, it is hypothesized that the boron added at the time of synthesis leaks out of the positive electrode active material particle and activates the condition on the surface of the positive electrode and increases the high-rate discharge performance rather than stabilizing the structure upon replacing Mn and Ni.

Furthermore, in the case of the active material that comprises the layer structure of the present invention, basically, the 6a site is occupied with Li, and the 6b is occupied with Mn, Ni, and Co, and the 6c site is occupied with O, but it is possible for the Li to be dispersed in the 6b site as well. In this case, Li has a monovalent valence; thus, the charge deficiency at 6b site can be increased and neutralized with an increase or a decrease of the 6c site.

In the above-mentioned Working Examples of the second embodiment, it is stated that $Li[Mn_{0.475}Ni_{0.475}B_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}V_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}Al_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}Mg_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}Co_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}Cr_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}Ti_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}Li_{0.05}O_2]$ [sic], are used as the main structural components of the positive electrode active material, but a similar effect can be achieved when other dissimilar elements M are used as well.

In the above-mentioned working examples of the third embodiment, it is stated to use $Li[Mn_{0.475}Ni_{0.475}B_{0.05}O_2]$, $Li[Mn_{0.475}Ni_{0.475}B_{0.05}O_2]$ [sic, repeated], $Li[Mn_{0.475}Ni_{0.474}V_{0.05}B_{0.001}O_2]$, $Li[Mn_{0.475}Ni_{0.474}V_{0.05}Al_{0.001}O_2]$, $Li[Mn_{0.475}Ni_{0.474}V_{0.05}Mg_{0.001}O_2]$, $Li[Mn_{0.475}Ni_{0.474}V_{0.05}Co_{0.001}O_2]$, $Li[Mn_{0.475}Ni_{0.474}Cr_{0.05}B_{0.001}O_2]$, $Li[Mn_{0.475}Ni_{0.474}Ti_{0.05}B_{0.001}O_2]$, having a high surface concentration of Boron as the main structural components of the positive electrode active material, but a similar effect can be achieved when other dissimilar elements M' are used as well.

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In the above-mentioned Working Examples of the fourth embodiment, it is stated that

$Li[Mn_{0.45}Ni_{0.45}Co_{0.01}O_2]$, $Li[Mn_{0.425}Ni_{0.425}Co_{0.1}B_{0.05}O_2]$, $Li[Mn_{0.425}Ni_{0.425}Co_{0.1}V_{0.05}O_2]$, $Li[Mn_{0.425}Ni_{0.425}Co_{0.1}Al_{0.05}O_2]$, $Li[Mn_{0.425}Ni_{0.425}Co_{0.1}Mg_{0.05}O_2]$, $Li[Mn_{0.425}Ni_{0.425}Co_{0.1}Cr_{0.05}O_2]$, $Li[Mn_{0.425}Ni_{0.425}Co_{0.1}Ti_{0.05}O_2]$, $Li[Mn_{0.425}Ni_{0.425}Co_{0.1}Li_{0.05}O_2]$,

are used as the main structural components of the positive electrode active material, but a similar effect can be achieved when other dissimilar elements are used as well.

In this case, working examples are explained with a nonaqueous secondary cells that utilize a synthetic graphite as the negative electrode material, and the same good effect was achieved with other negative electrode materials as well.

Furthermore, the present invention is not limited to the above-mentioned starting raw material activated material, manufacturing method, positive electrode, negative electrode, electrolyte, separator, shape of the cell, etc.

<Field of industrial application>

The present invention is to eliminate the above-mentioned existing problems, and production of a secondary cell with high energy density exhibiting an excellent high-rate charging/discharging performance and high charging/discharging cycle performance is made possible.

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Claims of Invention

1. A positive electrode active material mainly comprising a Li-Mn-Ni type composite oxide, and the positive electrode active material is characterized by the fact that the specific surface of the Li-Mn-Ni composite oxide measured by the BET method is 0.3 m^2/g or above and 1.5 m^2/g or below.

2. The positive electrode active material described in Claim 1 above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide is the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$.

3. The positive electrode active material described in 1 above characterized by the fact

that a part of Mn and Ni that comprise the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and is a composite oxide with a composition indicated by the following general formula.

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

(Wherein, M is the aforementioned dissimilar element;

x=0.001 to 0.1 ; x'=0.001 to 0.1 ;

y=0 to 0.1 ; y'=0 to 0.1 ;

$x+x'+y+y' \leq 0.4$; $0 \leq z \leq 1$)

4. The positive electrode active material described in the Claim 1 above characterized by the fact that a part of Mn and Ni that comprises the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and is a composite oxide with a composition indicated by the following general formula.

$Li_{1-z}[Mn_{0.5-x-y}Ni_{0.5-x'-y'}M_{x+x'}Li_{y+y'}O_2]$

(Wherein, M is the aforementioned dissimilar element;

x=0.01 to 0.1 ; x'=0.01 to 0.1 ;

y=0 to 0.1 ; y'=0 to 0.1 ;

$x+x'+y+y' \leq 0.2$; $0 \leq z \leq 1$)

5. The positive electrode active material described in the aforementioned Claim 3 or Claim 4 characterized by the fact that the aforementioned dissimilar element M is one or more elements selected from the group consisting of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, and Zn.

[p. 72]

6. The positive electrode active material described in Claim 1 above characterized by the fact that a part of Mn and Ni that comprise the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and

boron and is a composite oxide with a composition indicated by the following general formula.

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

(Wherein, M' is the aforementioned dissimilar element;

r=0.001 to 0.1 ; r'=0.001 to 0.1 ;

s=0 to 0.1 ; s'=0 to 0.1 ;

$r+r'+s+s'+w+w' \leq 0.4$;

w+w'=0.0005 to 0.01 ; $0 \leq t \leq 1$)

7. The positive electrode active material described in Claim 1 above characterized by the fact that a part of Mn and Ni that structures the composite oxide indicated by $LiMn_{0.5}Ni_{0.5}O_2$ in the aforementioned Li-Mn-Ni type composite oxide is replaced with a dissimilar element and boron and is a composite oxide with the composition indicated by the following general formula.

$Li_{1-t}[Mn_{0.5-r-s-w}Ni_{0.5-r'-s'-w'}B_{w+w'}M'_{r+r'}Li_{s+s'}O_2]$

(Wherein, M' is the aforementioned dissimilar element;

r=0.01 to 0.1 ; r'=0.01 to 0.1 ;

s=0 to 0.1 ; s'=0 to 0.1 ;

$r+r'+s+s'+w+w' \leq 0.2$;

w+w'=0.0005 to 0.01 ; $0 \leq t \leq 1$)

8. The positive electrode active material described in Claim 6 or Claim 7 above characterized by the fact that the aforementioned dissimilar element M' is one or more elements selected from the group consisting of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, and Zn.

9. The positive electrode active material described in the Claim 1 above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide is a composite oxide indicated by $Li[Mn_cNi_dCo_eLi_aM''_b]O_2$ (Wherein, M'' is an element other than Mn, Ni, Co or Li, $d \leq c+e+a+b$, $c+d+e+a+b=1$, $0 \leq a \leq 0.05$, $0 \leq b \leq 0.05$, $0.2 \leq c \leq 0.05$, $0.02 \leq e \leq 0.4$).

[p. 73]

10. The positive electrode active material described in the Claim 9 above characterized by

the fact that the aforementioned M" is one or more elements selected among the group consisting of B, Mg, Al, Ti, V, Cr, Fe, Co, Cu, and Zn.

11. The positive electrode active material described in one of Claim 1 to Claim 10 above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide has a layer crystalline structure having peaks at $2\theta = 18.6\pm1°$, $36.6\pm1°$, $37.8\pm1°$, $38.2\pm1°$, $44.3\pm1°$, $48.4\pm1°$, $58.4\pm1°$, $64.2\pm1°$, $64.8\pm1°$, $68.8\pm1°$ on the X-ray diffraction chart that utilizes CuKα ray.

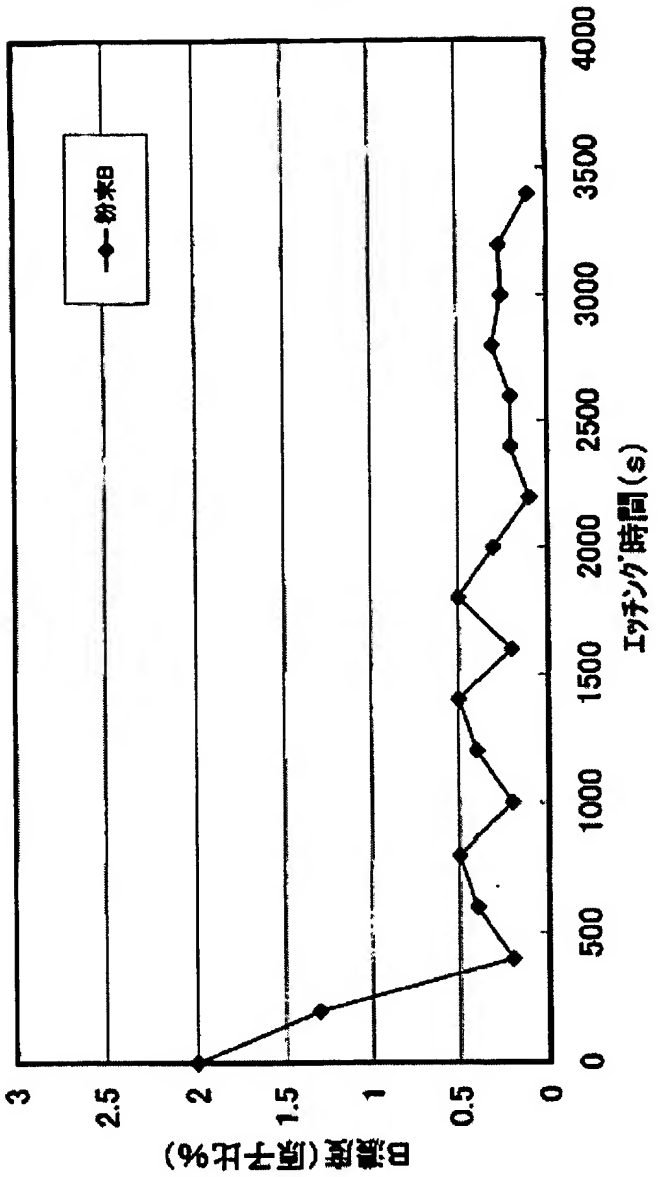
12. The positive electrode active material described in one of Claim 1 to Claim 11 above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide has a relative intensity ratio of the diffraction peak of $2\theta=44.1\pm1°$ for the diffraction peak of $2\theta=18.6\pm°$ on the powder X-ray diffraction chart that utilizes CuKα rays.

13. The positive electrode active material described in one of Claim 1 to Claim 12 above characterized by the fact that the aforementioned Li-Mn-Ni type composite oxide has the half-bandwidth of the diffraction peak at $2\theta=18.6\pm1°$ in the range of 0.13° to 0.20° and the half band width of the diffraction peak at $2\theta=44.1\pm1°$ in the range of 0.10° to 0.17° on the powder X-ray diffraction chart that utilizes CuKα rays.

14. The positive electrode active material described in one of Claim 1 to Claim 13 above characterized by the fact that the particle diameter of the aforementioned Li-Mn-Ni type composite oxide is in the range of 3 μm to 20 μm.

15. The nonaqueous secondary cell that utilizes the positive electrode active material described in one of Claim 1 to Claim 14 above.

Fig. 1



B Concentration (atomic %)

Horizontal axis: Etching time (s)

Solid diamonds: Powder B

Fig. 2

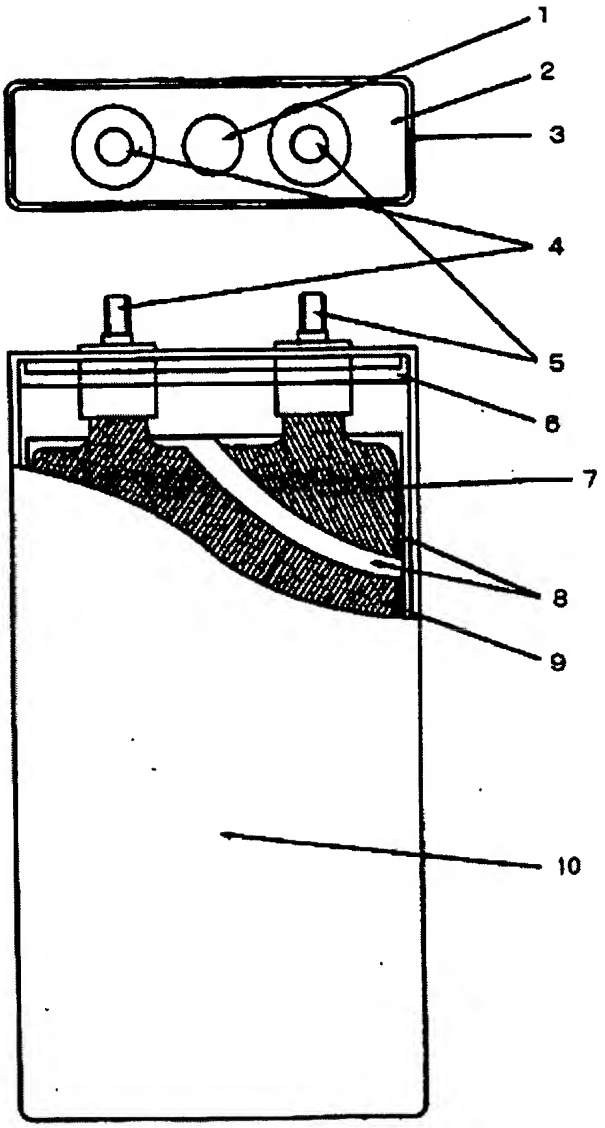
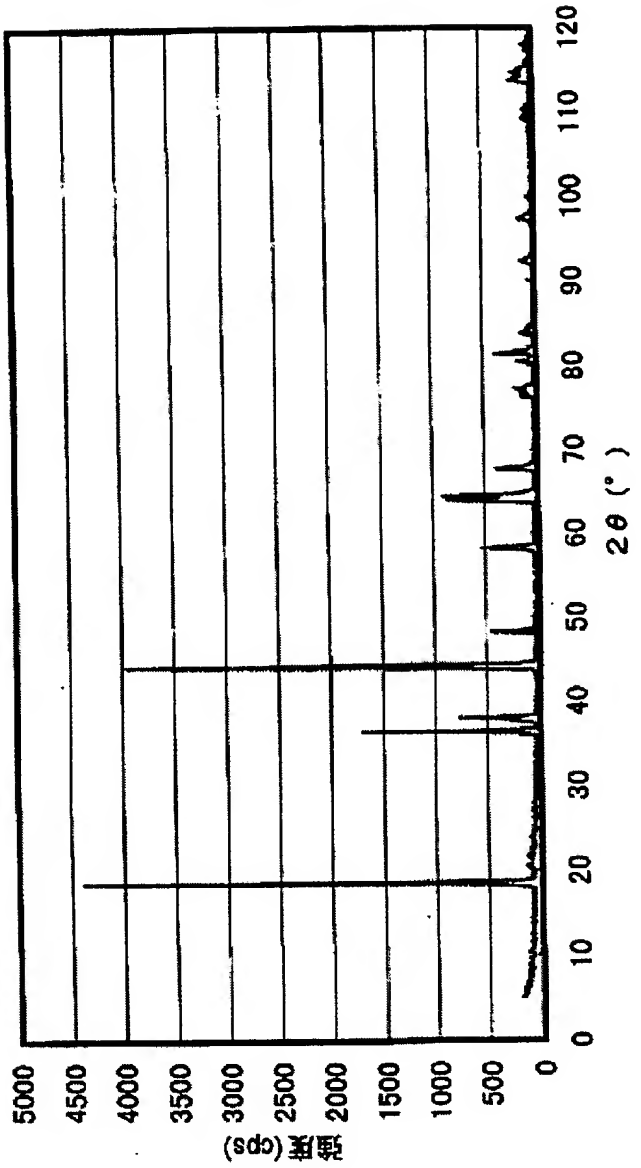
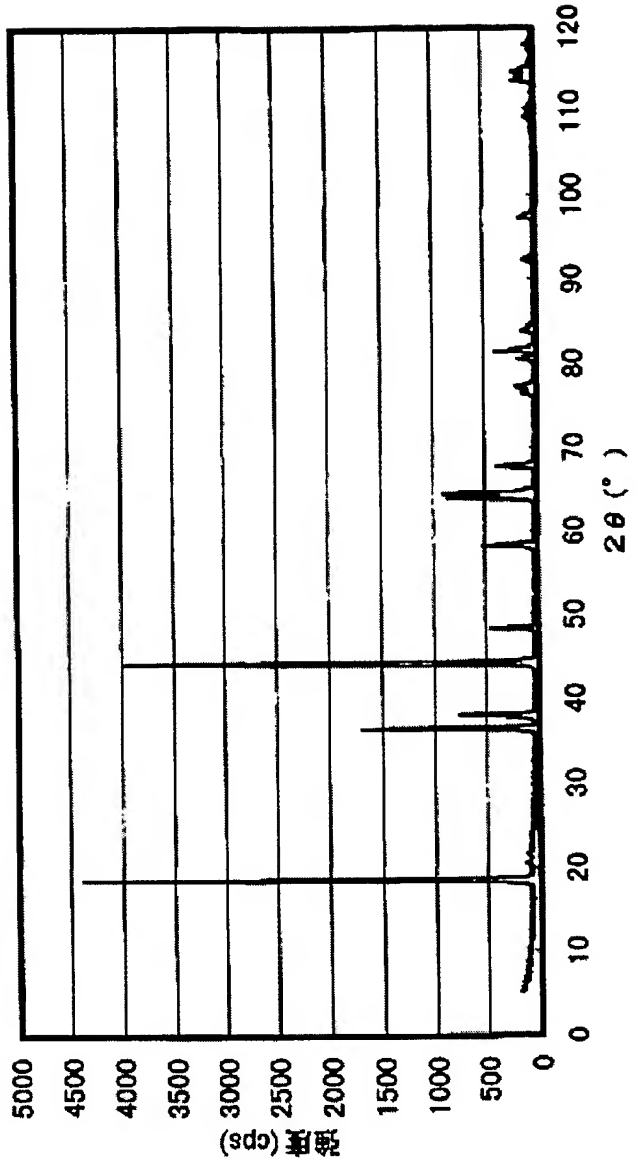


Fig. 3



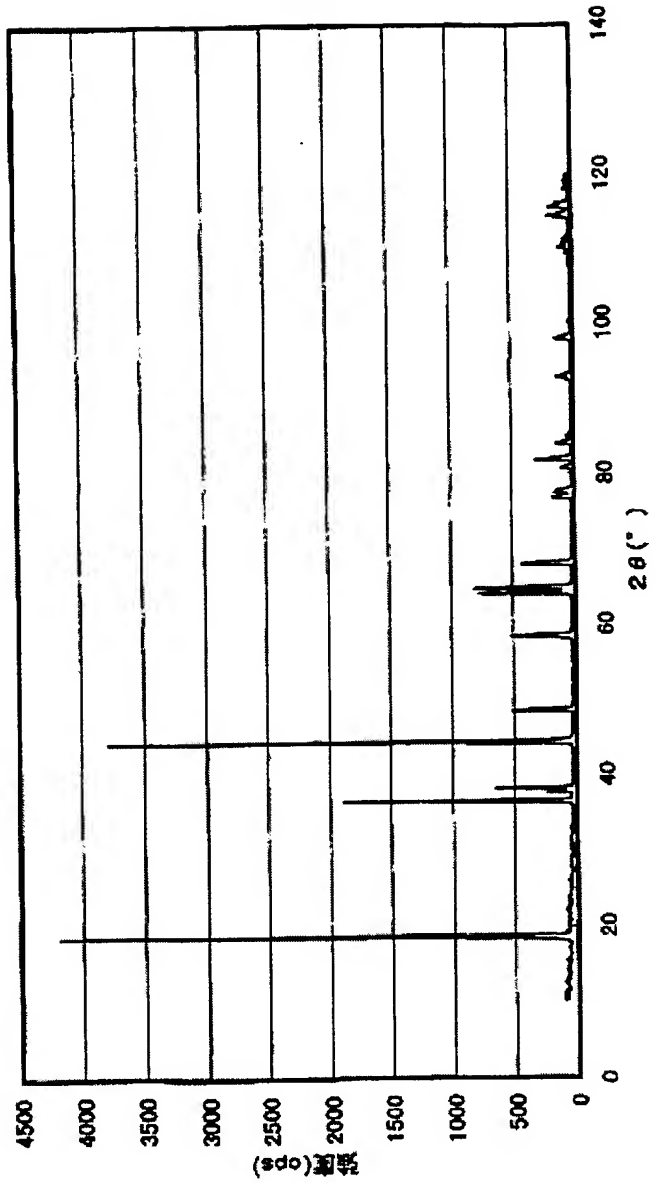
Intensity (cps)

Fig. 4



Intensity (cps)

Fig. 5



Intensity (cps)

Fig. 6

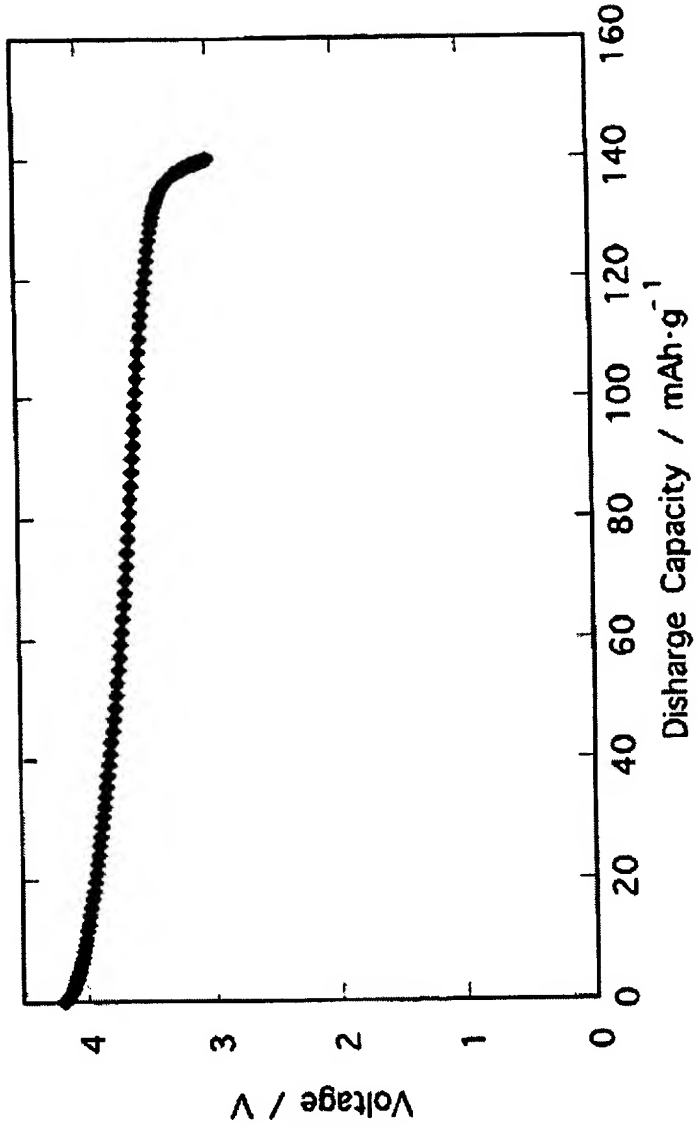

Voltage / V
4
3
2
1
0
Disharge Capacity / mAh·g-1
0
20
40
60
80
100
120
140
160

Fig. 7

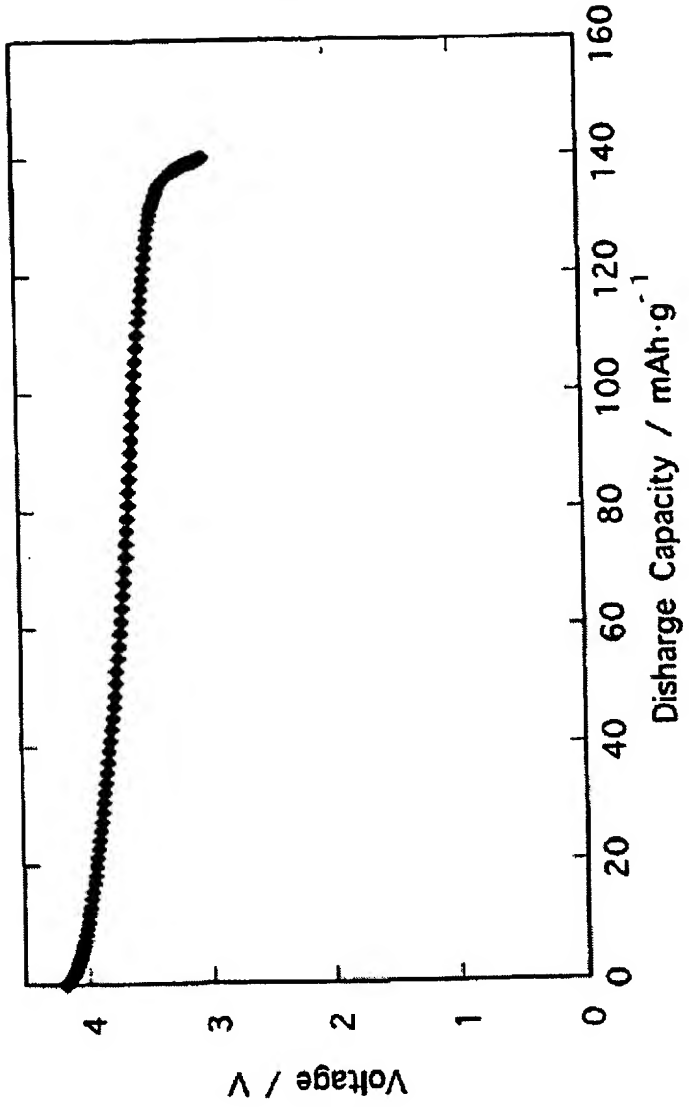
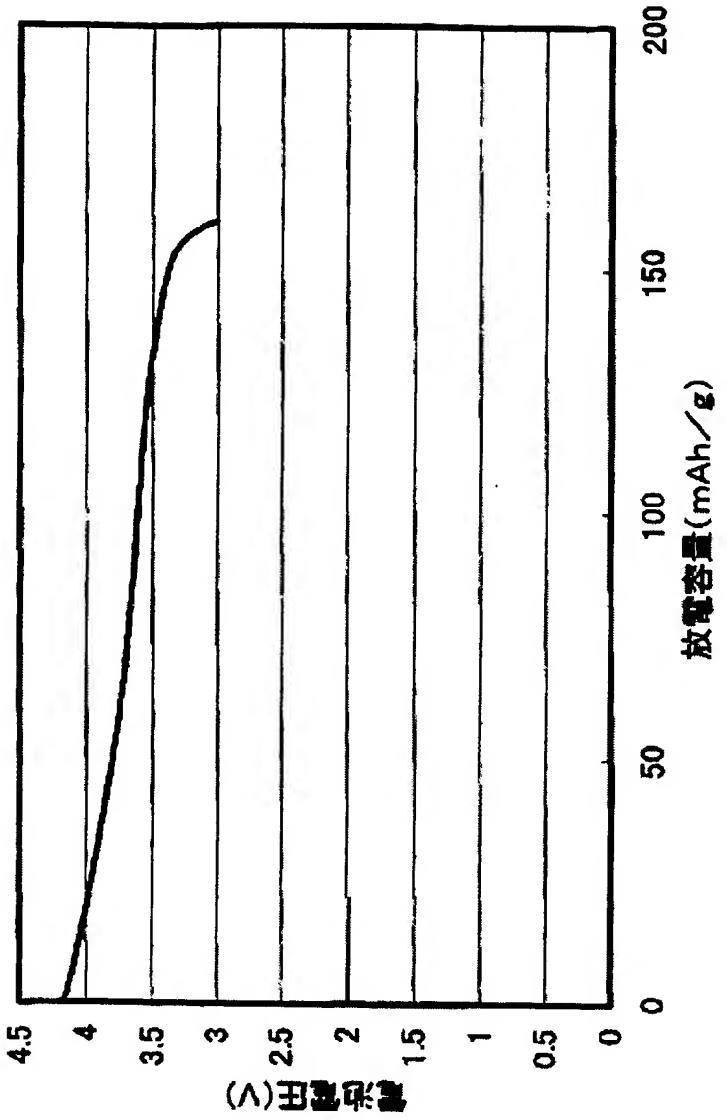

Voltage / V
4
3
2
1
0
Disharge Capacity / mAh·g-1
0
20
40
60
80
100
120
140
160

Fig. 8



Cell Voltage (V)

Horizontal axis: Charge capacity (mAh/g)